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CONCEPTS AND METHODS FOR DESCRIBING CRITICAL PHENOMENA IN FLUIDS

J. V. SENGERS AND

J. M. H. LEVELT SENGERS

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16. Abstract

A survey is presented of current concepts and methods for describing equilibrium critical phenomena in fluids. The predictions of theoretical models for a critical-point phase transition in fluids, namely, the classical equation with third-degree critical isotherm, that with fifth-degree critical isotherm, and the lattice gas, are reviewed. We discuss the renormalization group theory of critical phenomena, developed in recent years, and the hypothesis of universality of critical behavior supported by this theory. We discuss the nature of the gravity effects and how they affect critical-region experimentation in fluids. The behavior of the thermodynamic properties and the correlation function is formulated in terms of scaling laws. The predictions of these scaling laws and of the hypothesis of universality of critical behavior are compared with experimental data for one-component fluids, and it is indicated how the methods can be extended to describe critical phenomena in fluid mixtures. For one-component fluids, we relate the scale factor of the correlation length to the two scale factors of the thermodynamic functions. The report concludes with a discussion of the relation between correlation length and equation of state of one-component fluids near the critical point.

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I. Introduction

This report will be concerned with the nature of the thermodynamic behavior of fluids in the vicinity of a critical point. We shall restrict ourselves to classical fluids which means that we shall not consider the superfluid transition in liquid helium. However, the gas-liquid critical regions of ^{3}He, ^{4}He and other light fluids do fall within the domain of this report. We shall begin with a discussion of the nature of a critical point from thermodynamic considerations. We shall then conclude this introduction with an outline of the subjects covered in this report.

According to Gibbs' phase rule, a one-component fluid has in general two thermodynamic degrees of freedom. However, when two phases of a one-component fluid coexist, only one degree of freedom is left. Since all intensive properties or "fields" are equal in the two coexisting phases, the condition of coexistence defines a curve in the space of the two independent field variables. On this coexistence curve, extensive properties or "densities", such as entropy and number density, are generally not the same in the two coexisting phases. The critical point, however, is an endpoint on a coexistence curve at which not only all fields but also all densities have become equal in the two fluid phases. The two phases can no longer be distinguished from each other and the coexistence curve terminates.

When two phases coexist in a two-component fluid, the system still has two thermodynamic degrees of freedom. The condition of coexistence then determines a two-dimensional surface in the three-dimensional space of independent field variables. On this coexistence surface the density

variables such as number density, entropy and concentration generally differ in the two coexisting phases. A coexistence surface may, however, end in a critical line at which not only all fields but also all densities of the coexisting phases are equal, i.e. the coexisting phases have become identical.

Critical points are focal points of exceptional thermodynamic behavior, not only when they are approached from within the two-phase region but also when approached from the one-phase region. They are points of incipient instability. Thermodynamic stability requires that the determinant of the matrix of second derivatives of the energy $U(S,V, \ldots)$ as a function of its characteristic extensive variables, entropy S, volume V, etc., be positive definite. For a one-component fluid this matrix has the form

$$\text{Stiffness Matrix} \quad \begin{pmatrix} \frac{\partial^2 U}{\partial S^2} & \frac{\partial^2 U}{\partial S \partial V} \\ \frac{\partial^2 U}{\partial S \partial V} & \frac{\partial^2 U}{\partial V^2} \end{pmatrix} = \begin{pmatrix} \frac{T}{C_V} & -\frac{T\alpha_P}{K_T C_V} \\ -\frac{T\alpha_P}{K_T C_V} & \frac{C_P}{VK_T C_V} \end{pmatrix}, \qquad (1.1)$$

where C_P and C_V are the heat capacities at constant pressure and constant volume, respectively, $\alpha_P = V^{-1}(\partial V/\partial T)_P$ the isobaric thermal expansion coefficient and $K_T = -V^{-1}(\partial V/\partial P)_T$ the isothermal compressibility. This matrix was called the stiffness matrix by Tisza [1961]. Tisza chose this wording to indicate an analogy with mechanics, where "stiffness" denotes the increase of stress when the system is strained. The analogy of strain in thermodynamics is a change in volume or entropy, and the increase of stress is the corresponding change in pressure

$P = -(\partial U/\partial V)_S$ or in temperature $T = (\partial U/\partial S)_V$. The determinant of the stiffness matrix is given by

$$D(S,V) = \frac{T}{VK_T C_V} \quad . \tag{1.2}$$

At the critical point the compressibility K_T diverges strongly, that is, at least as fast as the inverse temperature difference with the critical point. Thus the determinant D(S,V) approaches zero at the critical point, indicating marginal stability.

Tisza also introduced the so-called compliance matrix whose elements are the second derivatives of -G(T,-P), where G is the Gibbs free energy.†

$$\text{Compliance Matrix} \quad \begin{pmatrix} -\frac{\partial^2 G}{\partial T^2} & \frac{\partial^2 G}{\partial T \partial P} \\ \frac{\partial^2 G}{\partial T \partial P} & -\frac{\partial^2 G}{\partial P^2} \end{pmatrix} = \begin{pmatrix} \frac{C_P}{T} & V\alpha_P \\ V\alpha_P & VK_T \end{pmatrix} \quad . \tag{1.3}$$

This choice of name again indicates an analogy with mechanics; the compliance is the strain of a mechanical system due to an increase in stress. The compliance matrix is the inverse of the stiffness matrix. Since the determinant of the stiffness matrix approaches zero, all elements of the compliance matrix diverge at the critical point. Thus the strong divergence of K_T implies similar divergences in α_p and C_p. It was discovered in the 1960's that the constant-volume heat capacity C_V of fluids diverges weakly at the critical point, that is, roughly as

---

† Note that G reduces to the chemical potential when taken per mole or per particle.

the logarithm of the difference between the actual temperature and that of the critical point. Thus the determinant of the compliance matrix,

$$D(T,P) = VK_T C_V/T \ , \tag{1.4}$$

diverges "strongly times weakly" in the language of Griffiths and Wheeler [1970]. In multicomponent fluids, the stiffness matrix contains the second derivatives of the energy with respect to all independent density variables. The determinant of the corresponding compliance matrix, however, diverges "strongly times weakly," just as that of a one-component fluid. The description of the thermodynamic anomalies in a fluid mixture, therefore, bears a close analogy to that in one-component fluids.

Closely associated with the marginal stability and diverging compressibility is the presence of large thermal fluctuations in the vicinity of the critical point (Klein and Tisza, 1949). These critical fluctuations in turn lead to anomalous behavior of various dynamical properties of fluids near critical points. The average size of a critical fluctuation is indicated by the correlation length. Near a critical point, this correlation length becomes much longer than the range of molecular interaction. The fluid behaves as a collection of "droplets" or aggregates of molecules of macroscopically fluctuating density, in which the individual molecular interactions are of less importance. Consequently, critical behavior shows considerable similarity in a large variety of fluids. This similarity is expressed by the term "universality" which we shall define precisely. The presence of a new length scale, the correlation length, gives thermodynamic

properties in the critical region a character of homogeneity. The homogeneity property makes it possible to reduce the number of independent variables by proper choice of scale.

Scaling is the main theme of this report. In Section II the concepts of homogeneity and scaling are introduced as properties of the theoretical models for critical point phase transitions. In Section III the scaling laws and the hypothesis of universality are formulated for the thermodynamic behavior of one-component fluids and compared with the experimental results. In Section IV the description is generalized to include fluid mixtures. In Section V the postulate of homogeneity is formulated for the correlation function and universality of the correlation functions, both with three and with two scale factors, is explored.

In this report we restrict ourselves to a review of the description of equilibrium critical phenomena in fluids. A survey of the behavior of transport properties of fluids near the critical point will be presented in a subsequent NASA contractor report.

In preparing this report we have benefitted from stimulating discussions with Drs. A. J. Bray, R. F. Chang, R. W. Gammon, M. S. Green, S. C. Greer, R. J. Hocken, P. C. Hohenberg and M. R. Moldover. The late Mr. T. A. Murphy assisted us by determining scaled equation of state parameters for a number of fluids. The research project was cosponsored by the U. S. Office of Standard Reference Data and by the Center of Materials Research at the University of Maryland.

II. Concepts for Describing Critical Phenomena in Fluids

2.1 Critical Exponents for Thermodynamic Properties

Let A be the Helmholtz free energy, S the entropy, μ the chemical potential per particle and ρ the number density. We also find it convenient to introduce a symmetrized isothermal compressibility χ_T as

$$\chi_T \equiv (\partial\rho/\partial\mu)_T = \rho^2\kappa_T \ . \tag{2.1}$$

The thermodynamic properties are made dimensionless by expressing them in units of appropriate combinations of the critical temperature T_c, the critical density ρ_c and the critical pressure P_c. Specifically, we define

$$\begin{aligned} &T^* = T/T_c, \ \rho^* = \rho/\rho_c, \ P^* = P/P_c \\ &A^* = A/VP_c, \ \mu^* = \mu\rho_c/P_c, \ \chi_T^* = \chi_T P_c/\rho_c^2 \\ &S^* = ST_c/VP_c, \ C_V^* = C_V T_c/VP_c \ . \end{aligned} \tag{2.2}$$

Note that the reduced extensive thermodynamic properties A^*, S^* and C_V^* are taken per unit volume. In addition we define the differences

$$\begin{aligned} \Delta T^* &= (T-T_c)/T_c \\ \Delta\rho^* &= (\rho-\rho_c)/\rho_c \\ \Delta\mu^* &= \{\mu(\rho,T)-\mu(\rho_c,T)\}\rho_c/P_c \ , \end{aligned} \tag{2.3}$$

where $\mu(\rho_c,T)$ is the chemical potential on the critical isochore at temperature T.

In the description of the anomalous critical behavior of a physical property it is assumed that sufficiently close to the critical point the

property varies as a simple power of the temperature difference or the density difference from the critical point. The exponent of the power law will depend on the property chosen, the path along which the critical point is approached and the way the distance from the critical point is measured. The most commonly used power laws for thermodynamic properties are summarized in Table I. The paths along which these power laws are defined, namely the critical isochore $\Delta\rho^* = 0$, the critical isotherm $\Delta T^* = 0$ and the coexistence curve $\Delta\rho^* = \Delta\rho^*_{cxc}$ are schematically indicated in Fig. 1 together with the corresponding exponents.

The critical exponents introduced in Table I are not all independent of each other. The laws of thermodynamics impose several rigorous inequalities between combinations of the "thermodynamic" exponents α, β, γ, δ, θ_p, θ_μ (Griffiths, 1965a,b, 1972; Rowlinson, 1969). In particular

$$
\begin{aligned}
&\text{(Griffiths, 1965a; Rushbrooke, 1965)} && 2-\alpha'' \leq \beta(\delta+1) \quad , \\
&\text{(Rushbrooke, 1963; Fisher, 1964)} && \alpha'' + 2\beta + \gamma' \geq 2, \\
&\text{(Liberman, 1966)} && \beta(\delta-1) \leq \gamma' \quad , \\
&\text{(Griffiths, 1965b)} && \theta_p \leq \alpha'' + \beta \quad , \\
&\text{(Mermin and Rehr, 1971)} && \theta_\mu \leq \alpha'' + \beta \quad .
\end{aligned}
\tag{2.4}
$$

Furthermore, the scaling hypothesis for thermodynamic properties, to be introduced in Section 3.2, leads to the exponent relations

$$
\begin{aligned}
&\alpha = \alpha' = \alpha'' = \theta_p \\
&\gamma = \gamma' \\
&2-\alpha = \beta(\delta+1) \\
&\gamma = \beta(\delta-1) \quad ,
\end{aligned}
\tag{2.5}
$$

so that only two thermodynamic exponents can be chosen independently.

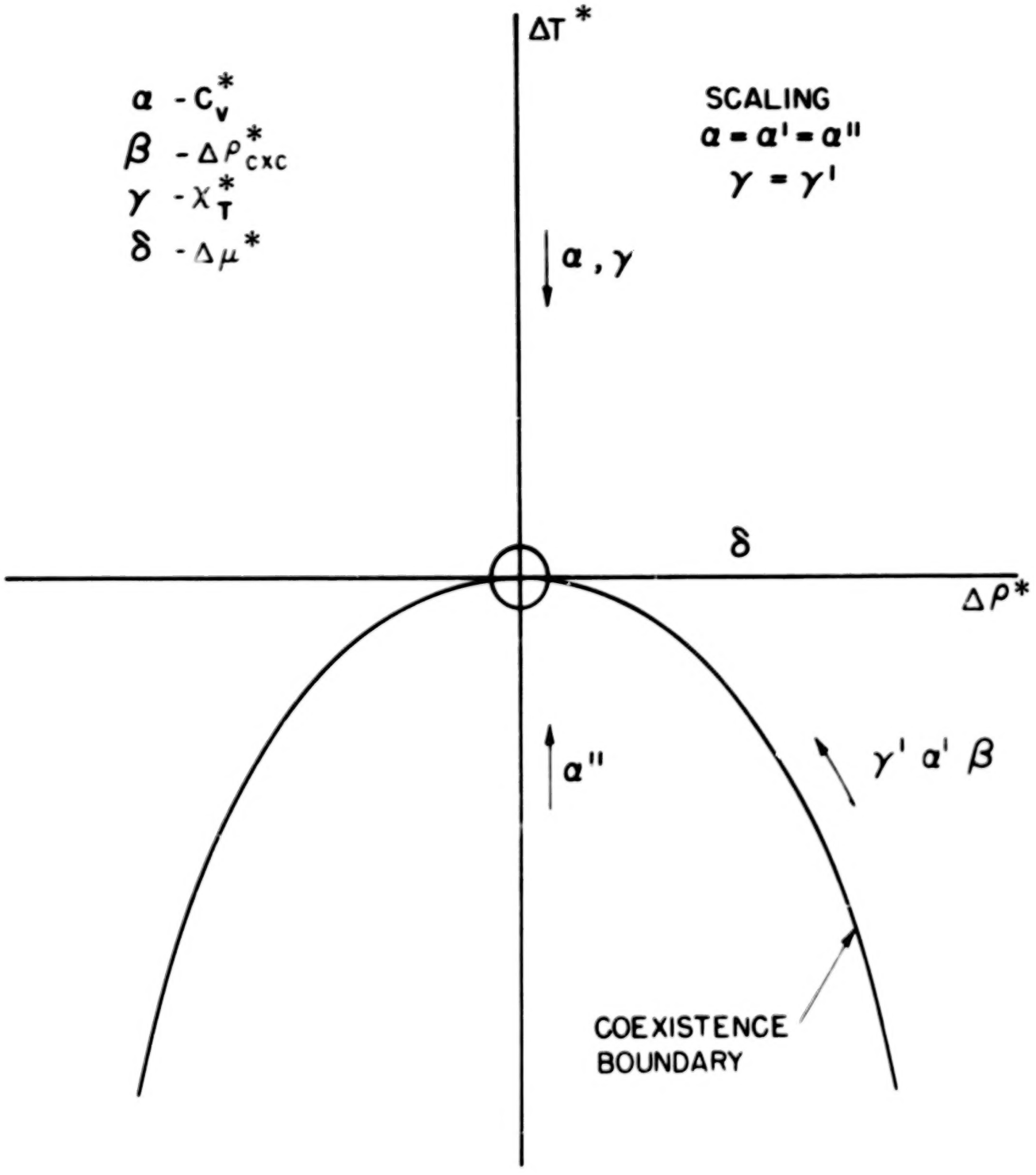

Figure 1. Special paths in the $\Delta\rho^*$ - ΔT^* plane and power law exponents defined along them.

Table I

Power Laws for Thermodynamic Properties

Path	Power Law
$T \leq T_c$, $\rho = \rho_{cxc}$	$\Delta\rho^*_{cxc} = \pm B\lvert\Delta T^*\rvert^{\beta}$
$T = T_c$	$\Delta\mu^* = D(\Delta\rho^*)\lvert\Delta\rho^*\rvert^{\delta-1}$
$T \geq T_c$, $\rho = \rho_c$	$\chi_T^* = \Gamma\lvert\Delta T^*\rvert^{-\gamma}$
$T \leq T_c$, $\rho = \rho_{cxc}$, one-phase	$\chi_T^* = \Gamma'\lvert\Delta T^*\rvert^{-\gamma'}$
$T \geq T_c$, $\rho = \rho_c$	$C_V^*/T^* = \frac{A^+}{\alpha}\{\lvert\Delta T^*\rvert^{-\alpha}-1\}$
$T \leq T_c$, $\rho = \rho_{cxc}$, one-phase	$C_V^*/T^* = \frac{A_I^-}{\alpha'}\{\lvert\Delta T^*\rvert^{-\alpha'}-1\}$
$T \leq T_c$, $\rho = \rho_c$, two-phase	$C_V^*/T^* = \frac{A_{II}^-}{\alpha''}\{\lvert\Delta T^*\rvert^{-\alpha''}-1\}$
$T \leq T_c$, two-phase	$d^2P^*_{cxc}/dT^{*2} \propto \lvert\Delta T^*\rvert^{-\theta_P}$
$T \leq T_c$, two-phase	$d^2\mu^*_{cxc}/dT^{*2} \propto \lvert\Delta T^*\rvert^{-\theta_\mu}$

2.2 A Model of a Critical-Point Phase Transition.

I. The Classical Equation with Third-Degree Isotherm

The first successful attempt at formulating an equation of state exhibiting a critical point was that of Van der Waals [1873]. The place of his work in the context of critical phenomena was recently commemorated at the Van der Waals centennial conference (Prins, 1974). The equation of Van der Waals is presently viewed as one of a large class of equations of state that are called classical or mean-field equations. Their common feature is that they assume an analytic dependence of the Helmholtz free energy or of the pressure on volume and temperature. While the critical point is characterized by the conditions $(\partial P/\partial V)_T = 0$, $(\partial^2 P/\partial V^2)_T = 0$ and $(\partial^3 P/\partial V^3)_T \neq 0$. Above the critical temperature, the pressure is a monotonically decreasing function of volume, so that the compressibility is positive and finite. At the critical point there is a horizontal inflection point on the P-V isotherm, at which point the compressibility diverges. Isotherms below the critical temperature exhibit a "loop," on part of which the pressure rises with volume, violating the condition for mechanical stability. The system then splits into two mechanically stable coexisting phases. The Maxwell equal area construction, which replaces the "loop" by a straight line parallel to the volume axis, ensures that the temperatures, pressures and chemical potentials of the two coexisting phases are equal.

Van der Waals' equation reads

$$(P + \frac{a}{\tilde{V}^2})(\tilde{V}-b) = RT\,, \tag{2.6}$$

where $\tilde{V}$ is the molar volume and R the molar gas constant. According

to this equation the critical behavior of the P-V isotherm comes about through competition between the hard core repulsion of the molecules, represented by the excluded volume term b, and the longer-range attraction between the molecules, represented by a pressure term a/V^2 or an internal energy term a/V. Van der Waals' approximation for the attractive interaction is rigorous in the limit of weak long-range intermolecular forces (Kac *et al.*, 1963; Uhlenbeck *et al*, 1963; Hemmer *et al.*, 1964; Van Kampen, 1964; Lebowitz, 1974). In real fluids, however, the attractive forces are usually not long range, as was realized by Van der Waals. This is the reason why the mean-field theories fail to represent the observed thermodynamic behavior near the critical point.

The horizontal inflection point for the Van der Waals equation is located at P_c, $\tilde{V}_c$, T_c with

$$P_c = \frac{a}{27b^2},\ \tilde{V}_c = 3b,\ RT_c = \frac{8a}{27b}\ .$$

If pressure, volume and temperature are measured in units of P_c, $\tilde{V}_c$ and T_c the *reduced* equation of state

$$(P^* + \frac{3}{V^{*2}})(V^* - \frac{1}{3}) = \frac{8}{3}T^* \qquad (2.7)$$

is obtained in which there is no explicit appearance of parameters characteristic of a particular substance. Van der Waals fluids have identical reduced equations of state and are said to obey the law of corresponding states.

As mentioned earlier, Van der Waals' equation is an example of a classical or mean-field equation of state which is analytic in volume and temperature at the critical point. Most equations of state used in

engineering applications are of this nature. All classical equations lead to a specific characteristic pattern of the critical anomalies. This pattern can be explored by studying the Taylor expansion of the classical equation around the critical point. Early investigations of this type were carried out by Van der Waals [1893,1894] and by Van Laar [1912]. Recent studies were made by Baehr [1963a,b], Barieau [1966, 1968], Levelt Sengers [1970] and Mulholland [1973].

Before developing the Taylor expansion a choice of variables has to be made. The relation between the variations of the field variables pressure P, temperature T and chemical potential μ is given by the Gibbs-Duhem equation

$$SdT - VdP + Nd\mu = 0 \ , \tag{2.8}$$

where N is the total number of molecules, if the chemical potential μ is taken per particle. In order to scale the conjugate extensive variables they are usually divided by N, or more specifically, by the number of moles N/N_o, where N_o is Avogadro's number. This procedure yields the relation

$$d\tilde{G} = -\tilde{S}dT + \tilde{V}dP \ , \tag{2.9}$$

where $\tilde{G}$, $\tilde{S}$ and $\tilde{V}$ are the molar values of the Gibbs free energy, entropy and volume, respectively. By a Legendre transformation one obtains the relation

$$d\tilde{A} = -\tilde{S}dT - PdV \tag{2.10}$$

for the Helmholtz free energy per mole $\tilde{A}(\tilde{V},T)$ as a function of *volume* and temperature. Differentiation of $\tilde{A}$ with respect to $\tilde{V}$ then yields an equation of state $P(\tilde{V},T)$ for the pressure as a function of $\tilde{V}$ and T. However, alternate but equivalent thermodynamic relations are obtained when the extensive properties in (2.8) are scaled by the volume V so that instead of (2.9)

$$dP = sdT + \rho d\mu \ , \tag{2.11}$$

where $s = S/V$ is the entropy density and $\rho = N/V$ the number density. A Legendre transformation then yields, instead of (2,10), a relation

$$d(A/V) = -sdT + \mu d\rho \tag{2.12}$$

for the Helmholtz free energy density A/V as a function of *density* and temperature. Differentiation of the Helmholtz free energy relation then leads to an equation of state $\mu(\rho,T)$ for the chemical potential as a function of density and temperature. From the point of view of thermodynamics the two methods of description are completely equivalent. In practice a description in terms of $P(\tilde{V},T)$ is often preferred because of the more direct accessibility of the variables to measurement. However, for real fluids near the critical point a description in terms of $\mu(\rho,T)$ deserves preference for reasons of increased symmetry to be discussed in Section 3.1. For this reason we shall formulate here the Taylor expansion of the Helmholtz free energy density in terms of ρ, rather than the more conventional expansion of the Helmholtz free energy per mole $\tilde{A}$ in terms of $\tilde{V}$. However, if desired, the interested reader can easily work out the analogous expansion for $\tilde{A}(\tilde{V},T)$.

Using the reduced variables defined in (2.2) the fundamental postulate of the classical theory can be formulated as

$$A^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!n!} A_{mn} (\Delta\rho^*)^m (\Delta T^*)^n$$

$$\mu^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!n!} \mu_{mn} (\Delta\rho^*)^m (\Delta T^*)^n \qquad (2.13)$$

$$P^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!n!} P_{mn} (\Delta\rho^*)^m (\Delta T^*)^n \ .$$

Since $\mu^* = (\partial A^*/\partial \rho^*)_T$ and $P^* = \mu^* \rho^* - A^*$, the expansion coefficients A_{mn}, μ_{mn} and P_{mn} are interrelated by

$$\mu_{m,n} = A_{m+1,n} \qquad (m \geq 0)$$

$$P_{m,n} = A_{m+1,n} + (m-1)A_{m,n} \qquad (m \geq 0) \qquad (2.14)$$

$$P_{m,n} = \mu_{m,n} + (m-1)\mu_{m-1,n} \qquad (m \geq 1) \ .$$

The conditions of criticality imply that

$$A_{20} = A_{30} = 0, \quad \mu_{10} = \mu_{20} = 0, \quad P_{10} = P_{20} = 0. \qquad (2.15)$$

We can arrange the expansion coefficients into matrices of the form

A_{mn}	1	ΔT^*	$(\Delta T^*)^2$	μ_{mn}	1	ΔT^*	$(\Delta T^*)^2$	P_{mn}	1	ΔT^*	$(\Delta T^*)^2$
1	A_{00}	A_{01}	A_{02}		μ_{00}	μ_{01}	μ_{02}		P_{00}	P_{01}	P_{02}
$\Delta\rho^*$	A_{01}	A_{11}	A_{12}		0	μ_{11}	μ_{12}		0	P_{11}	P_{12}
$(\Delta\rho^*)^2$	0	A_{21}	A_{22}		0	μ_{21}	μ_{22}		0	P_{21}	P_{22}
$(\Delta\rho^*)^3$	0	A_{31}	A_{32}		μ_{30}	μ_{31}	μ_{32}		P_{30}	P_{31}	P_{32}
$(\Delta\rho^*)^4$	A_{40}	A_{41}	A_{42}		μ_{40}	μ_{41}	μ_{42}		P_{40}	P_{41}	P_{42}

(2.16)

with

$$
\begin{aligned}
&\mu_{00} = A_{10} \quad , \quad P_{00} = A_{10} - A_{00} = P_c^* = 1 \\
&\mu_{30} = A_{40} \quad , \quad P_{30} = A_{40} = \mu_{30} \\
&\mu_{40} = A_{50} \quad , \quad P_{40} = A_{50} + 3A_{40} = \mu_{40} + 3\mu_{30} \\
&\mu_{01} = A_{11} \quad , \quad P_{01} = A_{11} - A_{01} \\
&\mu_{11} = A_{21} \quad , \quad P_{11} = A_{21} = \mu_{11} \\
&\mu_{21} = A_{31} \quad , \quad P_{21} = A_{31} + A_{21} = \mu_{21} + \mu_{11}
\end{aligned}
\tag{2.17}
$$

We assume here that $P_{30} = \mu_{30} = A_{40} \neq 0$. This is the case of "three-point contact" between the critical isobar and the critical isotherm in the terminology of Baehr, since both the first derivative $(\partial P/\partial\rho)_T$ and the second derivative $(\partial^2 P/\partial\rho^2)_T$ vanish at the critical point, but not the third derivative $(\partial^3 P/\partial\rho^3)_T$. It is also possible to construct a classical equation of state in which $P_{30} = \mu_{30} = A_{40} = 0$. Thermodynamic stability then requires that $P_{40} = \mu_{40} = A_{50} = 0$ as well. If then $P_{50} = \mu_{50} = A_{60} \neq 0$ we obtain the case of "five-point contact" to be discussed in Section 2.3. In the case of "three-point contact" mechanical stability requires $P_{30} = \mu_{30} = A_{40}$ to be positive. For the

compressibility to be positive at temperatures above T_c the coefficient P_{11} must be positive as well. Thermal stability requires A_{02} to be negative.

We first obtain the values of the critical exponents δ, γ and α. The asymptotic shape of the critical isotherm ($\Delta T^* = 0$) follows immediately from the form of the matrix (2.16).

$$P^* - P_c^* = \mu^* - \mu_c^* = \frac{1}{6} P_{30} (\Delta\rho^*)^3 + \ldots , \tag{2.18}$$

so that $\delta = 3$ and $D = P_{30}/6$. For the compressibility χ_T^* along the critical isochore ($\Delta\rho^* = 0$, $\Delta T^* \geq 0$) we find

$$\chi_T^{*-1} = (\partial\mu^*/\partial\rho^*)_T = P_{11} \Delta T^* + \ldots , \tag{2.19}$$

so that $\gamma = 1$ and $\Gamma = P_{11}^{-1}$. The specific heat C_V^* along the critical isochore ($\Delta\rho^* = 0$, $T^* \geq 0$) is given by

$$C_V^*/T^* = -(\partial^2 A^*/\partial T^{*2})_\rho = -A_{02} + \ldots . \tag{2.20}$$

The specific heat C_V^* in the one-phase region remains finite and $\alpha = 0$.

As a next step we construct the two-phase region. For this purpose we consider the lowest-order terms in the expansions of the pressure and the chemical potential

$$P^* = P_c^* + P_{01}(\Delta T^*) + P_{11}(\Delta\rho^*)(\Delta T^*) + \frac{1}{6} P_{30}(\Delta\rho^*)^3 + \ldots \tag{2.21}$$

$$\mu^* = \mu_c^* + \mu_{01}(\Delta T^*) + \mu_{11}(\Delta\rho^*)(\Delta T^*) + \frac{1}{6} \mu_{30}(\Delta\rho^*)^3 + \ldots .$$

The term linear in ΔT^* changes sign at T_c. Its negative slope below T_c causes the appearance of the "Van der Waals loop". The system then splits into a vapor and a liquid phase such that

$$P_{vap} = P_{liq},\ \mu_{vap} = \mu_{liq},\ T_{vap} = T_{liq}\ , \tag{2.22}$$

while $\Delta\rho^*_{vap} \neq \Delta\rho^*_{liq}$. To lowest order we find for the coexisting phases

$$P_{11}(\Delta\rho^*_{vap})(\Delta T^*) + \frac{1}{6} P_{30}(\Delta\rho^*_{vap})^3 = P_{11}(\Delta\rho^*_{liq})(\Delta T^*) + \frac{1}{6} P_{30}(\Delta\rho^*_{liq})^3\ , \tag{2.23}$$

Since $\mu_{11} = P_{11}$ and $\mu_{30} = P_{30}$, the condition $\mu_{vap} = \mu_{liq}$ does not give any new information to this order. The condition (2.23) may be rearranged to read

$$\frac{(\Delta\rho^*_{liq} + \Delta\rho^*_{vap})^2 - (\Delta\rho^*_{liq})(\Delta\rho^*_{vap})}{\Delta T^*} = -\frac{6P_{11}}{P_{30}}\ . \tag{2.24}$$

Since the right-hand side of (5.2.24) is independent of temperature, we conclude that to lowest order $\Delta\rho^*_{liq}$ and $\Delta\rho^*_{vap}$ must vary as $|\Delta T^*|^{1/2}$. Thus the top of the coexistence curve is quadratic, that is $\beta = 1/2$.

Algebraic consistency leads us then to expect that the coexisting densities can be expanded in powers of $|\Delta T^*|^{1/2}$ so that (Van Laar, 1912)

$$\Delta\rho^*_{liq,vap} = B_1^{\pm}|\Delta T^*|^{1/2} + B_2^{\pm}|\Delta T^*| + B_3^{\pm}|\Delta T^*|^{3/2} + \ldots\ , \tag{2.25}$$

where the + sign refers to the liquid and the - sign to the vapor branch of the coexistence curve. When this equation is substituted into the expansions (2.21) for pressure and chemical potential, the coefficients of (2.25) are then determined by the condition that in each order the pressures and chemical potentials of the two branches are to be the same. We thus find (Levelt Sengers, 1970)

$$B = B_1^+ = -B_1^- = (6\mu_{11}/\mu_{30})^{\frac{1}{2}} = (6P_{11}/P_{30})^{\frac{1}{2}} , \tag{2.26a}$$

$$B_2 = B_2^+ = B_2^- = \frac{\mu_{21}}{\mu_{30}} - \frac{3\mu_{11}\mu_{40}}{5\mu_{30}^2} = \frac{P_{21}}{P_{30}} + \frac{4P_{11}}{5P_{30}} - \frac{3P_{11}P_{40}}{5P_{30}^2} , \tag{2.26b}$$

and

$$\Delta\rho_{liq,vap} = \pm B_1|\Delta T^*|^{\frac{1}{2}} + B_2|\Delta T^*| + \ldots . \tag{2.27}$$

We conclude that the coexistence curve has a quadratic top which is *symmetric*. For the sum of the two coexisting densities we find

$$\frac{(\Delta\rho^*_{liq} + \Delta\rho^*_{vap})}{2} = B_2|\Delta T^*| + \ldots . \tag{2.28}$$

Asymptotically, this sum is linear in the temperature. For the classical equation this "law of the rectilinear diameter" is a direct consequence of the assumed analyticity of the equation of state. It therefore not only applies in terms of the density, but it would also apply in terms of volume.

For the compressibility in the one-phase region along the coexistence curve we find

$$\chi_T^{*-1} = \mu_{11}\Delta T^* + \tfrac{1}{2}\mu_{30}(\Delta\rho^*_{liq,vap})^2 + \ldots = 2P_{11}|\Delta T^*| + \ldots , \tag{2.29}$$

so that $\gamma' = 1$ and $\Gamma' = (2P_{11})^{-1}$. The specific heat in the one-phase region along the coexistence curve reduces asymptotically again to (2.20), so that $\alpha' = 0$.

Finally, we consider the pressure $P^*_{cxc} = P^*_{liq} = P^*_{vap}$ and the chemical potential $\mu^*_{cxc} = \mu^*_{liq} = \mu^*_{vap}$ in the two-phase region obtained when the expansion (2.27) is substituted into (2.21)

$$P^*_{cxc} = P_{00} + P_{01}\Delta T^* + \tfrac{1}{2}\left[P_{02} + \frac{P_{11}^2}{P_{30}}\left(\frac{16}{5} - 2\frac{P_{21}}{P_{11}} + \frac{3P_{40}}{5P_{30}}\right)\right](\Delta T^*)^2 + \ldots$$

$$\mu^*_{cxc} = \mu_{00} + \mu_{01}\Delta T^* + \tfrac{1}{2}\left[\mu_{02} + \frac{\mu_{11}^2}{\mu_{30}}\left(-2\frac{\mu_{21}}{\mu_{11}} + \frac{3\mu_{40}}{5\mu_{30}}\right)\right](\Delta T^*)^2 + \ldots . \qquad (2.30)$$

We note that the coefficient of the term proportional to $|\Delta T^*|^{3/2}$ vanishes. An algebraic proof that only integer powers of ΔT^* contribute to the vapor pressure $P^*_{cxc}(T^*)$ and the saturation chemical potential $\mu^*_{cxc}(T)$ was recently given by Mulholland [1973].

For the pressure and chemical potential along the critical isochore ($\Delta\rho^* = 0$) above the critical temperature we find

$$P^*(\Delta\rho^* = 0, \Delta T^* \geq 0) = P_{00} + P_{01}\Delta T^* + \tfrac{1}{2}P_{02}(\Delta T^*)^2 + \ldots$$
$$\mu^*(\Delta\rho^* = 0, \Delta T^* \geq 0) = \mu_{00} + \mu_{01}\Delta T^* + \tfrac{1}{2}\mu_{02}(\Delta T^*)^2 + \ldots . \qquad (2.31)$$

On comparing this with (2.30) we thus conclude

$$\frac{dP^*_{cxc}}{dT^*} = \left(\frac{\partial P^*}{\partial T^*}\right)_{\rho_c}, \quad \frac{d\mu^*_{cxc}}{dT^*} = \left(\frac{\partial \mu^*}{\partial T^*}\right)_{\rho_c}. \qquad (2.32)$$

The vapor pressure below the critical temperature and the pressure along the critical isochore above the critical temperature have the same limiting slope, as already demonstrated by Van der Waals [1900].

On the other hand, the second derivatives $(\partial^2 P^*/\partial T^{*2})_{\rho_c}$ and $(\partial^2 \mu^*/\partial T^{*2})_{\rho_c}$ change discontinuously at the critical point

$$\frac{d^2 P^*_{cxc}}{dT^{*2}} - \left(\frac{\partial^2 P^*}{\partial T^{*2}}\right)_{\rho_c} = \frac{P_{11}^2}{P_{30}}\left\{\frac{16}{5} - 2\frac{P_{21}}{P_{11}} + \frac{3P_{40}}{5P_{30}}\right\} \tag{2.33a}$$

$$\frac{d^2 \mu^*_{cxc}}{dT^{*2}} - \left(\frac{\partial^2 \mu^*}{\partial T^{*2}}\right)_{\rho_c} = \frac{\mu_{11}^2}{\mu_{30}}\left\{-2\frac{\mu_{21}}{\mu_{11}} + -\frac{3\mu_{40}}{5\mu_{30}}\right\} . \tag{2.33b}$$

Using a thermodynamic relation of Yang and Yang [1964]

$$\frac{C_V^*}{T^*} = \left(\frac{\partial^2 P^*}{\partial T^{*2}}\right)_\rho - \rho^*\left(\frac{\partial^2 \mu^*}{\partial T^{*2}}\right)_\rho , \tag{2.34}$$

we find that the specific heat, on crossing the phase boundary from the one-phase region at the critical density, increases discontinuously by an amount

$$(C_V^*/T^*)_{II} - (C_V^*/T^*)_I = 3P_{11}^2/P_{30} . \tag{2.35}$$

The principal results for the classical equation with three-point contact are summarized in Table II. In Table III we present values that the coefficients in the power law expansion for the various properties assume in the case of Van der Waals' equation.

Table II

Properties of the Classical Equation with 3-Point Contact

Taylor expansions (one-phase)

$$\mu^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{\mu_{mn}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad \mu_{10} = \mu_{20} = 0, \ \mu_{30} > 0$$

$$P^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{P_{mn}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad P_{10} = P_{20} = 0, \ P_{30} > 0$$

$$A^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{A_{m,n}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad A_{20} = A_{30} = 0, \ A_{40} > 0$$

(For relations between coefficients, see (2.12.)

Critical exponents	Amplitudes
$\alpha = \alpha' = \alpha'' = 0$	
$\beta = \frac{1}{2}$	$B = (3!\mu_{11}/\mu_{30})^{\frac{1}{2}}$
$\gamma = \gamma' = 1$	$\Gamma = P_{11}^{-1}, \ \Gamma' = \frac{1}{2}P_{11}^{-1}$
$\delta = 3$	$D = P_{30}/3!$
$\theta_P = \theta_\mu = 0$	

Coexistence curve

$$\Delta\rho^*_{cxc} = \pm B|\Delta T^*|^{\frac{1}{2}} + B_2|\Delta T^*| \pm B_3|\Delta T^*|^{\frac{3}{2}} + \ldots$$

$$B_2 = \frac{\mu_{21}}{\mu_{30}} - \frac{3\mu_{11}\mu_{40}}{5\mu_{30}^2}$$

Vapor pressure

$$P^*_{cxc} = 1 + P_{01}\Delta T^* + P_2|\Delta T^*|^2 + \ldots$$

$$P_2 = \tfrac{1}{2}P_{02} + \frac{8P_{11}^2}{5P_{30}} - \frac{P_{11}P_{21}}{P_{30}} + \frac{3P_{11}^2P_{40}}{10P_{30}^2}$$

Table II (Continued)

Saturation chemical potential $\mu^*_{cxc} = \mu_{00} + \mu_{01}\Delta T^* + \mu_2(\Delta T^*)^2 + \ldots$	$\mu_2 = \frac{1}{2}\mu_{02} - \frac{\mu_{11}\mu_{21}}{\mu_{30}} + \frac{3\mu_{11}^2\mu_{40}}{10\mu_{30}^2}$
Specific heat ($\rho = \rho_c$, $T \leq T_c$) $C_V^*/T^* = C_0 + C_1\Delta T^* + \ldots$	$C_C = -A_{02} + \frac{3\mu_{11}^2}{\mu_{30}}$

TABLE III

Coefficients of Power Laws for Van der Waals' Equation

$$P^* = 8\rho^*T^*/(3-\rho^*) - 3\rho^{*2}$$

Compressibility	$\Gamma = \frac{1}{6}$, $\Gamma' = \frac{1}{12}$
Critical Isotherm	$D = \frac{3}{2}$
Coexistence Curve	$B = 2$, $B_2 = \frac{2}{5}$
Vapor Pressure	$P_{01} = 4$, $P_2 = \frac{24}{5}$
Saturation Chemical Potential	$\mu_2 = -\frac{6}{5}$
Jump in C_V at $\rho = \rho_c$	$(C_V^*/T^*)_{II} - (C_V^*/T^*)_I = 12$

2.3 A Model of a Critical-Point Phase Transition.

II. The Classical Equation with Fifth-Degree Isotherm

At the turn of the century it became evident that equations of the Van der Waals' type did not predict correctly the asymptotic shape of the coexistence curve and the critical isotherm of real fluids. Verschaffelt [1900] found that the coexistence curve of isopentane is approximately cubic while the critical isotherm is of a degree slightly larger than 4. Therefore, Verschaffelt [1901, 1904, 1923] and Wohl [1914] attempted to formulate equations of state with $\beta = 1/3$ and $\delta = 4$. However, the nonanalytic character of these equations was very troubling to engineers. A historical study of the early determinations of the values for the critical exponents was recently made by one of the authors (Levelt Sengers, 1976). Because of the reluctance to accept nonanalytic equations of state, attempts were made, first by Van Laar [1912] and subsequently by Plank [1936], to formulate an analytic equation that has a flatter coexistence curve and critical isotherm than equations of the Van der Waals' type. This goal was achieved by setting not two but four derivatives of P with respect to V equal to zero at the critical point. The most extensive study of this case was made by Baehr [1963a,b] who revealed some of its surprising features.

The expansion of A^*, μ^* and P^* have the same form as (2.13) and the relations between the coefficients are again given by (2.14). However, the conditions for criticality are now

$$\begin{aligned} A_{20} &= A_{30} = A_{40} = A_{50} = 0 \\ \mu_{10} &= \mu_{20} = \mu_{30} = \mu_{40} = 0 \\ P_{10} &= P_{20} = P_{30} = P_{40} = 0 \quad , \end{aligned} \tag{2.36}$$

while $P_{50} = \mu_{50} = A_{60} > 0$ and $P_{11} = \mu_{11} > 0$. The equation for the critical isotherm is

$$P^* - P_c^* = \mu^* - \mu_c^* = \frac{1}{120} P_{50} (\Delta\rho^*)^5 + \ldots , \tag{2.37}$$

so that $\delta = 5$ and $D = P_{50}/120$. The behavior of the compressibility along the critical isochore is the same as in the case of three-point contact so that $\gamma = 1$ and $\Gamma = P_{11}^{-1}$. The coexistence curve to lowest order is now determined by the condition

$$\frac{P_{50}}{5!}(\Delta\rho^*_{liq})^5 + P_{11}(\Delta\rho^*_{liq})(\Delta T^*) = \frac{P_{50}}{5!}(\Delta\rho^*_{vap})^5 + P_{11}(\Delta\rho^*_{vap})(\Delta T^*) . \tag{2.38}$$

Following the same reasoning as before, one finds

$$\Delta\rho^*_{liq,vap} = \pm B|\Delta T^*|^{\frac{1}{4}} + B_2|\Delta T^*|^{\frac{1}{2}} \pm B_3|\Delta T^*|^{\frac{3}{4}} + \ldots , \tag{2.39}$$

with

$$B = \left(\frac{5!P_{11}}{P_{50}}\right)^{\frac{1}{4}} , \tag{2.40a}$$

$$B_2 = \frac{B^2}{4}\left(\frac{\mu_{21}}{3\mu_{11}} - \frac{\mu_{60}}{7\mu_{50}}\right) = \frac{B^2}{4}\left(\frac{P_{21}}{3P_{11}} - \frac{P_{60}}{7P_{50}} + \frac{8}{21}\right) . \tag{2.40b}$$

Thus $\beta = \frac{1}{2}$, while the sum of the coexistence densities becomes

$$\tfrac{1}{2}(\Delta\rho^*_{liq} + \Delta\rho^*_{vap}) = B_2|\Delta T^*|^{\frac{1}{2}} + \ldots . \tag{2.41}$$

The law of the rectilinear diameter is no longer valid for this classical equation, neither in terms of density nor in terms of volume.

Table IV

Properties of the Classical Equation with 5-point Contact

Taylor expansions (one-phase)

$$\mu^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{\mu_{mn}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad \mu_{10} = \mu_{20} = \mu_{30} = \mu_{40} = 0$$

$$P^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{P_{mn}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad P_{10} = P_{20} = P_{30} = P_{40} = 0$$

$$A^* = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{A_{m,n}}{m!n!} (\Delta\rho^*)^m (\Delta T^*)^n; \quad A_{20} = A_{30} = A_{40} = A_{50} = 0$$

(For relations between coefficients see (2.14.)

Critical exponents

$\alpha = \alpha' = 0, \ \alpha'' = \frac{1}{2}$

$\beta = \frac{1}{4}$

$\gamma = \gamma' = 1$

$\delta = 5$

$\theta_P = \theta_\mu = \frac{1}{2}$

Amplitudes

$B = (5!\mu_{11}/\mu_{50})^{\frac{1}{4}}$

$\Gamma = P_{11}^{-1}, \ \Gamma' = \frac{1}{2}P_{11}^{-1}$

$D = P_{50}/5!$

Coexistence curve

$$\Delta\rho^*_{cxc} = \pm B|\Delta T^*|^{\frac{1}{4}} + B_2|\Delta T^*|^{\frac{1}{2}} \pm B_3|\Delta T^*|^{\frac{3}{2}} + \ldots$$

$$B_2 = \frac{B^2}{4}\left(\frac{\mu_{21}}{3\mu_{11}} - \frac{\mu_{60}}{7\mu_{50}}\right)$$

Vapor pressure

$$P^*_{cxc} = 1 + P_{01}\Delta T^* + P_{3/2}|\Delta T^*|^{\frac{3}{2}} + \ldots$$

$$P_{3/2} = B^2\left(\frac{P_{11}P_{60}}{42P_{50}} - \frac{P_{21}}{6} + \frac{8P_{11}}{21}\right)$$

Table IV (Continued)

Saturation chemical potential $\mu^*_{cxc} = \mu_{00} + \mu_{01}\Delta T^* + \mu_{3/2}\lvert\Delta T^*\rvert^{3/2} + \ldots$	$\mu_{3/2} = B^2\left(\frac{\mu_{11}\mu_{60}}{42\mu_{50}} - \frac{\mu_{21}}{6}\right)$
Specific heat ($\rho = \rho_c$, $T \leq T_c$) $C_V^*/T^* = \frac{A_{II}^-}{\alpha''}\lvert\Delta T^*\rvert^{-1/2}$	$A_{II}^- = \mu_{11}B^2/8$

For the compressibility along the coexistence curve one finds $\gamma' = 1$ and $\Gamma' = (4P_{11})^{-1}$. The temperature expansions for the vapor pressure and the saturation chemical potential become

$$P^*_{cxc} = P_{00} + P_{01}\Delta T^* + B^2\left(\frac{P_{11}P_{60}}{42P_{50}} - \frac{P_{21}}{6} + \frac{8P_{11}}{21}\right)\lvert\Delta T^*\rvert^{3/2} + \ldots,$$

$$\mu^*_{cxc} = \mu_{00} + \mu_{01}\Delta T^* + B^2\left(\frac{\mu_{11}\mu_{60}}{42\mu_{50}} - \frac{\mu_{21}}{6}\right)\lvert\Delta T^*\rvert^{3/2} + \ldots. \qquad (2.42)$$

Thus the slopes of the pressure and the chemical potential along the critical isochore and the saturation curve are still continuous at the critical point. However, in contrast to the case of three-point contact, the second derivatives $d^2P^*_{cxc}/dT^{*2}$ and $d^2\mu^*/dT^{*2}$ and hence C_V^*/T^* in the two-phase region now diverge as $\lvert\Delta T^*\rvert^{-1/2}$, so that $\theta_P = \theta_\mu = \alpha'' = 1/2$. Of course $\alpha = \alpha' = 0$, since the Helmholtz free energy is analytic in the one-phase region. The properties of the classical equation with five-point contact are summarized in Table IV.

2.4 Generalized Homogeneous Functions

The modern description of the thermodynamic behavior of a system near a critical point is based on the assumption of homogeneity of the basic thermodynamic functions. To introduce the concept of homogeneous functions we consider here functions of two variables only; generalization to functions of more variables is obvious.

A function f(u,v) of two variables u and v is called a generalized homogeneous function if it satisfies the relation (Stanley, 1971, 1972)

$$f(\lambda^{a_u} u, \lambda^{a_v} v) = \lambda f(u,v) \tag{2.43}$$

for two fixed exponents a_u and a_v and for all values of the parameter λ. It is noted that a relation of the type $f(\lambda^{a_u} u, \lambda^{a_v} v) = \lambda^p f(u,v)$ can always be reduced to the form (2.43) by a proper redefinition of the parameter λ.

When a function has the property of homogeneity one can always deduce a scaling law, i.e. the dependence on the two variables can be reduced to the dependence on one new variable by an appropriate change of scale. For this purpose we take $\lambda^{a_u} = u^{-1}$ so that

$$\frac{f(u,v)}{u^{1/a_u}} = f\left(1, \frac{v}{u^{a_v/a_u}}\right) , \tag{2.44a}$$

where, for simplicity, we consider only positive values of the variables u and v. Hence, the function f(u,v) after scaling with the factor u^{1/a_u} becomes a function of the single variable $v/u^{a_v/a_u}$. Another possible choice is $\lambda^{a_v} = v^{-1}$ so that

$$\frac{f(u,v)}{v^{1/a_v}} = f\left(\frac{u}{v^{a_u/a_v}},1\right) . \qquad (2.44b)$$

From (2.44) we note that a generalized homogeneous function satisfies a simple power law along any line $u/v^{a_u/a_v} = B$

$$f(u,v) = f(B,1)v^{1/a_v} , \qquad (2.45)$$

where $f(B,1)$ is a constant coefficient. In particular along the special lines $u = 0$ and $v = 0$ the function behaves as

$$f(0,v) = f(0,1)v^{1/a_v}, \quad f(u,0) = f(1,0)u^{1/a_u} . \qquad (2.46)$$

2.5 Homogeneity and Scaling Property of Classical Equations

In this section we consider to what extent in the vicinity of the critical point the classical equation of state becomes a generalized homogeneous function of the independent thermodynamic variables and satisfies a scaling law.

As mentioned in Section 2.1 thermodynamics imposes a number of inequality relationships between the critical exponents. Of the five exponent relations given in (2.4) we find that three are obeyed with the equal sign for both classical equations, namely $2 - \alpha'' = \beta(\delta+1)$, $\beta(\delta-1) = \gamma'$ and $\alpha'' + 2\beta + \gamma' = 2$. The other two relations, $\theta_p \leq \alpha'' + \beta$ and $\theta_\mu \leq \alpha'' + \beta$, are obeyed as inequalities, since for the case of three-point contact $\theta_p = \theta_\mu = \alpha'' = 0$ and for the case of five-point contact $\theta_p = \theta_\mu = \alpha'' = \frac{1}{2}$. We further note that in the case of three-point contact $\gamma = \gamma' = 1$, $\alpha = \alpha' = \alpha'' = 0$, while in the case of five-point contact $\gamma = \gamma' = 1$, $\alpha = \alpha' = 0$, $\alpha'' = \frac{1}{2}$.

To formulate the scaling property of the classical equation we develop our arguments again in terms of the equation of state for $\mu(\rho,T)$. We do stress, however, that for the classical equations the same arguments would hold for any choice of variables, including $P(\tilde{V},T)$ and $P(\rho,T)$. The Taylor expansions of the classical equations read to lowest order

$$\mu^* - \mu_c^* = \mu_{01}\Delta T^* + \frac{1}{3!}\mu_{30}(\Delta\rho^*)^3 + \mu_{11}(\Delta\rho^*)(\Delta T^*) \ ,$$

(three-point contact)

$$\mu^* - \mu_c^* = \mu_{01}\Delta T^* + \frac{1}{5!}\mu_{50}(\Delta\rho^*)^5 + \mu_{11}(\Delta\rho^*)(\Delta T^*) \ .$$

(five-point contact) (2.47)

It is convenient to define

$$\Delta\mu^* = \mu^* - \mu_c^* - \mu_{01}\Delta T^* \ . \tag{2.48}$$

Introducing the critical exponents $\delta = 3$, $\beta = \frac{1}{2}$ (three-point contact) and $\delta = 5$, $\beta = \frac{1}{4}$ (five-point contact) both equations (2.47) can be rearranged as

$$\Delta\mu^* = D(\Delta\rho^*)^\delta \left[1 + \frac{1}{x_0}\frac{\Delta T^*}{(\Delta\rho^*)^{1/\beta}}\right] \ , \tag{2.49}$$

where D and $x_0 = B^{-1/\beta}$ are readily expressible in terms of μ_{mn}. Hence to lowest order $\Delta\mu^*$ does indeed satisfy the homogeneity property (2.43) $\Delta\mu^*(\lambda^{a_\rho}\Delta\rho^*, \lambda^{a_T}\Delta T^*) = \lambda\Delta\mu^*(\Delta\rho^*, \Delta T^*)$ with $a_\rho = 1/\delta$ and $a_T = 1/\beta\delta$. If $\Delta\mu^*$ is "scaled" by $(\Delta\rho^*)^\delta$

$$\frac{\Delta\mu^*}{(\Delta\rho^*)^\delta} = D(1 + x/x_0) , \tag{2.50}$$

the result is a function of orly one independent scaling variable $x = \Delta T^*/(\Delta\rho^*)^{1/\beta}$.

The homogeneity and scaling properties of the nonanalytic equations of state will be discussed extensively in Section III. Here it is appropriate to point out the limitations of scaling for the classical equations. The quantity $\Delta\mu^*$ defined in (2.48) is equal to $\mu^*(\rho,T) - \mu^*(\rho_c,T)$ above T_c to linear order in ΔT^*. Since the chemical potential $\mu^*(\rho_c,T)$ along the critical isochore and the saturation chemical potential μ^*_{cxc} have continuous slopes, $\Delta\mu^*$ is also equal to $\mu^*(\rho,T) - \mu^*_{cxc}$ below T_c to lowest order in ΔT^*. Thus the scaled equation (2.50) is valid in the one-phase region both above and below T_c to linear order in ΔT^*. However the argument cannot be extended to include higher order terms in ΔT^*. If, for instance, in the case of three-point contact the term $\frac{1}{2}\mu_{02}(\Delta T^*)^2$ is added to (2.47) and then included in the definition of $\Delta\mu^*$, the quantity $\Delta\mu^* \neq \mu^*(\rho,T) - \mu^*_{cxc}$ below T_c, since the second derivative of $\mu^*(\rho_c,T)$ is discontinuous at the critical point. Alternatively, if all terms contributing on the $(\Delta T^*)^2$ level to μ^*_{cxc} are included in (2.47) the feature of homogeneity is lost. Thus although the classical equations of state obeys a scaling law to lowest order, its second derivative, and consequently the specific heat, in general do not scale even in lowest order.

2.6 A Model of a Critical-Point Phase Transition

III. Ising Model and Lattice Gas

Lenz and Ising formulated a model for the ferromagnetic phase transition in solids in which the assumption of long-range forces implicit in the classical or mean-field theories was dropped (Ising, 1925). In this Ising model, magnetic spins are placed on a regular array, one spin at each site, which may either point "upwards" or "downwards." In the simplest form of the model, the interactions between spins are limited to nearest neighbors only. These interactions may be ferromagnetic, when the lowest energy state is that of parallel spins on neighboring sites, or antiferromagnetic, when it is energetically favorable for neighboring spins to line up in an antiparallel configuration. Lenz and Ising were only able to solve the one-dimensional version of the model. However, in one dimension the system remains paramagnetic at all finite temperatures and does not exhibit a phase transition to a ferromagnetic state. The reason is that only one pair of opposite spins is enough to destroy the macroscopic magnetic moment.

In the 2- and 3-dimensional versions of the model a phase transition does occur (Peierls, 1936; Griffiths, 1972). Moreover, the 2-dimensional Ising model in zero magnetic field can be solved exactly as first achieved by Onsager [1944], who showed that the specific heat at constant field $H = 0$ diverges logarithmically at the critical point. This result was in direct contradiction with the assumption of analyticity of the Helmholtz free energy at the critical point in the classical theory.

The importance of the Ising model is enhanced by the fact that it can serve as a model for a variety of phase transitions (Green and Hurst, 1964). We have already seen that by changing the sign of the nearest-neighbor interaction both the ferromagnetic and the antiferromagnetic phase transitions can be described. If spins pointing upwards are replaced by particles A, while spins pointing downwards are replaced by particles B, we obtain a model for phase transitions in binary solids. If the energetically favorable configuration is that of unlike nearest neighbors, the order-disorder phase transition in binary alloys can be modeled. If the configuration with like nearest neighbors is more favorable, demixing in the solid phase can be described. To the extent that a liquid can be approximated by a lattice model, we obtain also a description of phase separation in partially miscible liquids. Finally, the Ising model can be used as a model for the gas-liquid transition. An early attempt in this direction was made by Cernuschi and Eyring [1939] who devised a so-called hole theory of liquids. The rigorous translation of the Ising model into a model for a gas on a lattice was formulated by Lee and Yang [1952].

In the ferromagnetic Ising model, a spin variable σ_i is assigned to each lattice site i, where σ_i can assume the value +1 or -1 depending on whether the spin points "up" or "down." The energy E of a microstate $\{\sigma_i\}$ is given by

$$E\{\sigma_i\} = -J \sum_{<i,j>} \sigma_i \sigma_j - H \sum_i \sigma_i \ , \qquad (2.51)$$

where J is an interaction constant and H the magnetic field and where the sum is to be taken over all pairs of nearest neighbors <ij>. The

partition function Z_s as a function of T, H and the total number of spins or sites N_s is then given by

$$Z_s(T,H,N_s) = \sum_{\{\sigma_i\}} \exp\left[\frac{J}{k_B T}\sum_{<ij>}\sigma_i\sigma_j + \frac{H}{k_B T}\sum_i \sigma_i\right], \tag{2.52}$$

where k_B is Boltzmann's constant. The (Gibbs) free energy F(H,T) is then obtained as

$$F = -k_B T \ln Z_s \tag{2.53}$$

To obtain a lattice gas each site is identified with the center of a cell with volume v_o such that

$$V = v_o N_s . \tag{2.54}$$

To each cell an occupancy variable τ_i is assigned such that $\tau_i = +1$ when the cell is occupied by a molecule and $\tau_i = 0$ when the cell is empty. Multiple occupancy is forbidden so as to account for the finite size of the molecules. To each pair of molecules in adjacent cells an attractive energy $-\varepsilon$ is assigned independent of the positions of the molecules within the cells. The energy of a microstate is then

$$E\{\tau_i\} = -\varepsilon \sum_{<ij>} \tau_i\tau_j , \tag{2.55}$$

and the partition function Z(T,V,N) of the lattice gas becomes

$$Z(T,V,N) = \left(\frac{v_o}{\Lambda^3}\right)^N \sum_{\{\tau_i\}}{}' \exp\left[\frac{\varepsilon}{k_B T}\sum_{<ij>}\tau_i\tau_j\right], \tag{2.56}$$

with $\Lambda = (h^2/2\pi m k_B T)^{\frac{1}{2}}$, where h is Planck's constant and m the molecular mass. The accent on the summation sign indicates that the summation is

restricted to microstates with $\Sigma\tau_i = N$. This awkward constraint is removed by considering the grand partition function

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} e^{N\mu/k_BT} = \sum_{\{\tau_i\}} \exp\left[\frac{\varepsilon}{k_BT}\sum_{<ij>}\tau_i\tau_j + \frac{\mu - k_BT\ln(\Lambda^3/v_o)}{k_BT}\sum_i \tau_i\right] . \tag{2.57}$$

The relation between the grand partition function Ξ of the lattice gas and the partition function Z_s of the Ising model is obtained by noting that $\tau_i = \frac{1}{2}(\sigma_i+1)$ so that $\sum_i \tau_i = \frac{1}{2}(\sum_i \sigma_i + N_s)$ and $\sum_{<ij>}\tau_i\tau_j = \frac{1}{4}\sum_{<ij>}\sigma_i\sigma_j + \frac{q}{2}\sum_i \sigma_i + \frac{1}{8}qN_s$, where q is the coordination number of the lattice. Hence, the grand partition function of the lattice gas can be written in the form

$$\Xi(T,V,\mu) = e^{(H-\frac{1}{8}qJ)N_s/k_BT}\, Z_s(T,H,N_s) , \tag{2.58}$$

with

$$\frac{\varepsilon}{4} = J , \tag{2.59}$$

$$\Delta\mu \equiv \mu + \frac{\varepsilon q}{2} - k_BT\ln\left(\frac{\Lambda^3}{v_o}\right) = 2H . \tag{2.60}$$

Since $PV = Pv_oN_s = k_BT\ln\Xi$, it also follows that

$$v_oP = (H - \tfrac{1}{8}qJ) - F/N_s . \tag{2.61}$$

Furthermore, since $\rho = \langle\sum_i \tau_i\rangle/V$ and $M/M_o = \langle\sum_i \sigma_i\rangle/N_s$, we find $2v_o\rho = 1 + M/M_o$, where M_o is the saturation magnetization of the ferromagnetic Ising model. At the critical point of the Ising model $M = 0$ so that for the lattice gas $\rho_c = 1/2v_o$ and

$$\Delta\rho^* = M/M_o = M^* . \tag{2.62}$$

On the critical isochore $M = 0$, the field $H = 0$ above and below T_c. Thus it follows from (2.60) that the chemical potential on the critical isochore of the lattice gas is given by

$$\mu(\rho_c,T) = k_B T \ln\left(\frac{\Lambda^3}{v_o}\right) - \frac{\varepsilon q}{2} , \tag{2.63}$$

and the quantity $\Delta\mu$ introduced in (2.60) may be identified with $\mu(\rho,T) - \mu(\rho_c,T)$. The properties of the lattice gas follow immediately from those of the Ising model via the relations given above (Fisher, 1966, 1967a).

The results obtained for the Ising model have been discussed in many places in the literature. Appropriate references may be found in the review papers of Fisher [1967a] and Domb [1974]. The values of the thermodynamic critical exponents for the 2-dimensional Ising model are $\alpha = \alpha'' = 0$, $\beta = 1/8$, $\gamma = \gamma' = 7/4$, $\delta = 15$; of these exponents α, β and γ are known exactly (Fisher, 1967a), while δ is known numerically to within 0.5% (Gaunt and Sykes, 1972).

The 3-dimensional Ising model has not been solved exactly, but many numerical results have been obtained from analyses of series expansions (Domb, 1974). The current exponent values deduced from series expansions are (Gaunt and Sykes, 1972, 1973; Gaunt and Guttman, 1974; Meijer and Farrell, 1975; Camp *et al.*, 1976):

$$\begin{aligned} &\alpha = 0.125 \pm 0.020, \quad \beta = 0.312 \pm 0.005, \\ &\gamma = 1.250 \pm 0.003, \quad \delta = 5.00 \pm 0.05 . \end{aligned} \tag{2.64}$$

independent of the lattice structure and the magnitude of the spin.

It is also believed that the values of the critical exponents do not change if the interactions extend beyond nearest neighbours as long as their range remains finite; it must be remarked, however, that the numerical evidence is not conclusive (Dalton and Wood, 1969; Farrell and Meijer, 1972). Anticipating that the critical exponents may turn out to be rational numbers, one frequently adopts as estimated values for the critical exponents of the 3-dimensional Ising model

$$\alpha = \alpha'' = \frac{1}{8},\ \beta = \frac{5}{16},\ \gamma = \gamma' = \frac{5}{4},\ \delta = 5\,. \tag{2.65}$$

The theoretical and numerical evidence gathered for the Ising model (as well as other lattice models) appears to be in accord with the postulate that the free energy is a generalized homogeneous function of temperature ΔT^* and $H^* = H/k_B T$. From this postulate it follows that the equation of state can be written in the form (Griffiths, 1967; Fisher, 1967b):

$$H^* = M^* |M^*|^{\delta-1} h_s(\Delta T^*/|M^*|^{1/\beta})\,. \tag{2.66}$$

An equation of this form for the 3-dimensional Ising model was originally proposed by Domb and Hunter [1965].

The equation of state for the lattice gas follows from (2.66) using (2.60) and (2.62). The properties of this equation of state will be discussed in Section 3.4. We also note from (2.62) that the chemical potential of the lattice gas is a regular function of temperature along the critica' isochore, in contrast to its behavior in the classical theory. From the Yang-Yang relation (2.34) it then follows that the anomaly in the specific heat C_V is equal to the anomaly in d^2P/dT^2 so that for the lattice gas $\alpha = \alpha'' = \theta_p$, while $\theta_\mu = 0$.

The regular behavior of $\mu(\rho_c,T)$ is a consequence of the particle-hole symmetry of the lattice gas. Since the Ising hamiltonian is invariant under reversal of the field H, while the magnetization M changes sign upon reversal of the field, we note that $\Delta\mu$ along an isotherm is antisymmetric with respect to the critical isochore

$$\Delta\mu^*(-\Delta\rho^*,\Delta T^*) = -\Delta\mu^*(\Delta\rho^*,\Delta T^*) \ . \tag{2.67}$$

As a consequence the derivative $\chi_T = \rho^2 K_T = (\partial\rho/\partial\mu)_T$ of the lattice gas is a symmetric function of $\Delta\rho^*$. The pressure P, however, given by (2.61), contains a symmetric and an antisymmetric term and therefore does not exhibit any special symmetry. In contrast to the classical equations, the equation of state for the chemical potential of the lattice gas has a symmetry which is absent in the equation of state for the pressure.

2.7 Renormalization Group Theory

On approaching a critical point a system exhibits large fluctuations in the order parameter (the magnetization near the Curie point of a spin system or the density near the gas-liquid critical point of a fluid). The range of these fluctuations is characterized by a correlation length ξ, a precise definition of which will be given in Section 5.1. For the systems under consideration this correlation length becomes much larger than the range of the intermolecular forces. Kadanoff [1966] gave a plausibility argument that the long range nature of the critical fluctuations causes the singular part of the free energy to become a generalized homogeneous function of its variables.

He also introduced the idea of universality: the critical singularities do not depend on those parameters in the hamiltonian that characterize the microscopic nature of the system on a length scale of the order of the intermolecular distances, but depend only on some gross features of the system such as the dimensionality of the system and the number of components of the order parameter (Kadanoff, 1966, 1971, 1976). These ideas have been given a firm theoretical basis by the renormalization group theory of critical phenomena, formulated by Wilson [1971] and further developed by many investigators.

In order to elucidate the method of the renormalization group theory, let us consider a generalization of the Ising model called Ising-like spin systems (Niemeijer and Van Leeuwen, 1976). An Ising-like spin system is a lattice system in which the interactions are not restricted to nearest neighbours only and in which the spin variable σ_i may assume an arbitrary number of values. In accordance with (2.53) the reduced free energy per spin $F^* = -F/N_s k_B T$ may be written in the form

$$F^* = \ln \sum_{\{\sigma_i\}} \exp \mathcal{H} , \tag{2.68}$$

where $\mathcal{H}$ is a generalized hamiltonian which depends on a number of parameters such as the temperature T, the field H, the number of states that the spin variable σ_i may assume, the interaction constants between nearest neighbours, next nearest neighbours, etc. These parameters may be formally indicated by the set of variables $\{K\} = K_1, K_2, \ldots$.

For a spin system with N_s lattice sites one may attempt to calculate the free energy from (2.68) by first summing only over groups that are within cells of length ℓ, where ℓ is measured in terms of the lattice constant. The result may then be interpreted in terms of the properties of a new spin system for which the lattice sites correspond to the cells of the original lattice. The number N_s' of this new spin system is related to the number N_s of the original lattice by $N_s'/N_s = \ell^{-d}$, where d is the dimensionality of the system. The reduced free energy $F^{*\prime}$ per spin of the new spin system may be written as

$$F^{*\prime} = F\{K'\} = \ln \sum_{\{\sigma_i'\}} \exp \mathcal{H}\{K'\} \ , \tag{2.69}$$

where the summation is to be conducted over all possible values of the spin variables σ_i' of the new spin system and where the hamiltonian $\mathcal{H}\{K'\}$ will be determined by a new set of values K_α' of the parameters of the hamiltonian. The transformation

$$\{K'\} = R_\ell\{K\} \tag{2.70}$$

is called a renormalization group transformation. It satisfies the semigroup property $R_{\ell_1} R_{\ell_2} = R_{\ell_1+\ell_2}$. Apart from an integration constant which is an analytic function of the parameters K_α, the free energy $F^*\{K'\}$ of the new spin system is related to the free energy $F^*\{K\}$ of the original system by (Niemeijer and Van Leeuwen, 1976)

$$F^*\{K\} = \ell^{-d} F^*\{K'\} \ . \tag{2.71}$$

Upon iteration of the renormalization transformation one traverses a trajectory in the space of the parameters of the hamiltonian. This

means that one is studying the system with respect to a length scale which becomes larger and larger. After having summed over the short range contributions the properties of the spin systems thus generated will vary little until one reaches a length scale comparable with the correlation length ξ. At the critical point, however, the correlation length is infinite. Hence, the crucial observation of the renormalization group theory is that for a system at a critical point the procedure always leads to a fixed point $\{K^*\}$ of the transformation at which

$$\{K^*\} = R_\ell\{K^*\}. \tag{2.72}$$

When the system is not at a critical point but close to it, the correlation length ξ is large but not infinite. Upon iteration of the renormalization transformation the trajectory in the space of the parameters of the hamiltonian will approach the fixed point as long as the length scale remains smaller than ξ and will move away from the fixed point when the length scale becomes larger than ξ. In the vicinity of the fixed point the transformation may be represented by a linear approximation

$$K_\alpha' - K_\alpha^* = \sum_\beta \left(\frac{\partial K_\alpha'}{\partial K_\beta}\right)_{K^*} (K_\beta - K_\beta^*) \ . \tag{2.73}$$

Let us denote the eigenvalues of the matrix $(\partial K_\alpha'/\partial K_\beta)_{K^*}$ (which are assumed to be real and positive) by ℓ^{y_α} and the corresponding eigenfunctions, usually referred to as scaling fields, by u_α (Wegner, 1972). Replacing the parameters K_α' by the scaling fields u_α, the transformation (2.73) in the vicinity of the fixed point reads

$$u_\alpha' = \ell^{y} u_\alpha \quad . \tag{2.74}$$

Hence, if we consider the free energy F as a function of the scaling fields u_α, it follows from (2.71) and (2.72) that in the vicinity of the critical point the free energy satisfies the relation

$$F^*(u_1,u_2, \ldots) = \ell^{-d} F^*(\lambda^{y_1}u_1,\lambda^{y_2}u_2, \ldots) \quad . \tag{2.75}$$

Thus the free energy becomes a generalized homogeneous function of the type defined in (2.43). The exponents y_α can be calculated by determining the eigenvalues of the linearized renormalization group transformation defined in (2.73). The relation (2.75) applies to that part of the free energy which we shall identify as the singular part F^*_{sing}. In addition there is a regular contribution due to the summations over the short range interactions.

The renormalization procedure is not restricted to lattice systems. In fact, most calculations based on the renormalization group theory have been performed for the so-called Landau-Ginzburg-Wilson model (Wilson, 1971; Wilson and Kogut, 1974). This model is a generalization of the Ising-like systems in which the spin variable σ_i is no longer associated with discrete lattice sites but is replaced by a spin function $\sigma(\vec{x})$ which is a continuous function of the position $\vec{x}$. The renormalization transformation is then obtained by integrating over those Fourier components of the spin function $\sigma(\vec{x})$ that correspond to wave lengths smaller than the corelation length ξ.

The scaling fields with $\ell^{y_\alpha} > 1$ (i.e. $y_\alpha > 0$) are called relevant and the scaling fields with $\ell^{y_\alpha} < 1$ (i.e. $y_\alpha < 0$) are called irrelevant. In some special cases one may also encounter a marginal

field with $\ell^{y_\alpha} = 1$. Upon iteration of the transformation (2.75) we conclude that the singular part of the free energy in the vicinity of the critical point will assume the same form independent of the starting values of the irrelevant parameters. For Ising-like systems of a given dimensionality $d < 4$, there are two relevant scaling fields which asymptotically may be identified with the field H^* and the temperature ΔT^*. Thus near the critical point the free energy satisfies the relation

$$F^*_{sing}(H^*,\Delta T^*) = \ell^{-d} F^*_{sing}(\ell^{y_1} H^*, \ell^{y_2} \Delta T^*). \tag{2.76}$$

Choosing ℓ such that $\ell^{y_1} = H^{*-1}$, we conclude that the singular part of the free energy satisfies a scaling law of the form

$$F^*_{sing}(H^*,\Delta T^*) = H^{*d/y_1} F^*_{sing}\left(\frac{\Delta T^*}{H^{*y_2/y_1}}, 1\right). \tag{2.77}$$

The renormalization group theory confirms that the singular behavior of the free energy, and thus of all thermodynamic properties, depends on only two critical exponents y_1 and y_2. Since $M^* = (\partial F^*/\partial H^*)_T$, one readily verifies that a scaled equation of state of the form postulated in (2.66) is recovered if the exponent β is identified with $(d-y_1)/y_2$ and the exponent δ with $y_1/(d-y_2)$. The renormalization group theory shows how these critical exponents can be calculated from the eigenvalues of the linearized renormalization group transformation. The scaling function of the free energy and other related properties can be obtained by studying their dependence on the parameters of the hamiltonian in the vicinity of the fixed point. For further details the reader is referred to the literature (Wilson, 1971; Wilson and Kogut, 1974; Ma, 1973,1976; Di Castro *et al.*, 1974; Schroer, 1974; Fisher, 1974; Van Leeuwen, 1975; Niemeijer and Van Leeuwen, 1976; Wallace, 1976).

An important consequence of the renormalization group theory is that all systems whose hamiltonians differ with respect to the irrelevant parameters only, will have the same critical exponents and the same scaling functions. Such systems are said to belong to the same universality class. It is widely assumed that universality classes for homogeneous, isotropic systems with short range forces may be assigned according to the spatial dimensionality and the number of components of the order parameter. Although the renormalization procedure has not yet been carried out for systems with hamiltonians resembling fluids, it is nevertheless expected that fluids near the gas-liquid critical point and binary liquids near the critical mixing point should belong to the same universality class as the Ising model and the Landau-Ginzburg-Wilson model (Hubbard and Schofield, 1972). This hypothesis will be further discussed in Sections 3.5 and 3.8.

Using the method of the renormalization group theory estimates have been obtained for the critical exponents of this universality class (Kadanoff *et al.*, 1976; Baker *et al.*, 1976; Golner and Riedel, 1975, 1976). The most accurate estimates appear to be those reported by Baker *et al.* for the Landau-Ginzburg-Wilson model. In particular they found for the critical exponents β and γ

$$\beta = 0.320 \pm 0.015, \qquad \gamma = 1.241 \pm 0.002 . \tag{2.78}$$

There exists a small unresolved discrepancy between the exponent values obtained for the Landau-Ginzburg-Wilson model on the basis of the renormalization group theory and the values (2.64) obtained for the Ising model from series expansions. We shall return to this point in Section 5.5.

2.7 Gravity Effects

Experimentation near a critical point is difficult because of the strong divergence in the thermal expansion coefficient and the compressibility and the slow rate of decay towards equilibrium. For a discussion of the type of thermodynamic information available and the experimental difficulties encountered the reader is referred to a review published elsewhere (Levelt Sengers, 1975). Here we restrict the discussion to one major feature encountered in all critical region experimentation with fluids, namely the effect of the earth's gravitational field.

As noted by Gouy [1892], near the gas-liquid critical point the compressibility becomes so large that gravity will induce an appreciable density gradient. We may assume that at each level h in the cell the local chemical potential $\mu(\rho_h,T)$ equals the chemical potential of a system with uniform density ρ_h at temperature T in the absence of gravity. Since in the presence of gravity the total chemical potential is the sum of the local chemical potential $\mu(\rho_h,T)$ and the gravitational potential mgh, we have

$$\mu(\rho_h,T) - \mu(\rho_{h_o},T) = -mg(h-h_o) \ , \tag{2.79}$$

where m is the molecular mass if the chemical potential is taken per particle. In terms of dimensionless quantities

$$\mu^*(\rho_h,T) - \mu^*(\rho_{h_o},T) = -\frac{h-h_o}{h_c} \ , \tag{2.80}$$

with

$$h_c = P_c/mg\rho_c \ . \tag{2.81}$$

In Table V we present values of the parameter h_c^{-1} for a number of fluids. Note that the gravity effect on the chemical potential will be proportional to h_c^{-1}. Thus at a given $\Delta\rho^*$ and ΔT^* the gravity effects in helium will be much larger than in steam. Since h_c is of the order of 10^5 cm, gravity will contribute on the 10^{-5} level to the chemical potential in cells with a height of about 1 cm. Since $(\partial\rho^*/\partial\mu^*)_T$ diverges, this small variation in μ^* will cause an appreciable density gradient. As an example we show in Fig. 2 the predicted size of such gravitationally induced density profiles in xenon at a number of temperatures. In binary liquids near the critical mixing point gravity will induce a concentration gradient (Yvon, 1937; Voronel and Giterman, 1965; Mistura, 1971).

Gravity effects impose serious limitations upon the information that can be obtained from conventional PVT experiments in the vicinity of the critical point. The experiments become unreliable when the average or bulk density as measured begins to deviate from the local density prevailing at the level where the pressure is measured. The magnitude of the range where the data are obscured by these effects depends on a variety of factors such as the height of the vessel, the value of h_c and the precision of the temperature control. Generally no accurate information is obtained from conventional PVT experiments in the temperature range $|\Delta T^*| < 5 \times 10^{-4}$.

However, gravity effects can be used to advantage if the density is measured as a function of height. In accordance with (2.80) such measurements yield ρ as a function of μ over a total pressure span of a few hundred Pascals, i.e. a few millibars. Thus a resolution of the equation of state can be obtained that is several orders beyond what is attainable with conventional techniques.

Table V

The Parameter $h_c^{-1} = m\rho_c g/P_c$ for a Number of Fluids

Fluid	$h_c^{-1} \times 10^3$ m^{-1}	Fluid	$h_c^{-1} \times 10^3$ m^{-1}
^3He	3.48	CO	0.84
^4He	3.00	CO_2	0.62
Ne	1.72	NH_3	0.20
Ar	1.08	N_2O	0.61
Kr	1.62	SF_6	1.90
Xe	1.86	CH_4	0.35
H_2	0.24	C_2H_4	0.42
N_2	0.91	C_2H_6	0.42
O_2	0.85	C_3H_8	0.51
H_2O	0.14	$CClF_3$	1.50
D_2O	0.16		

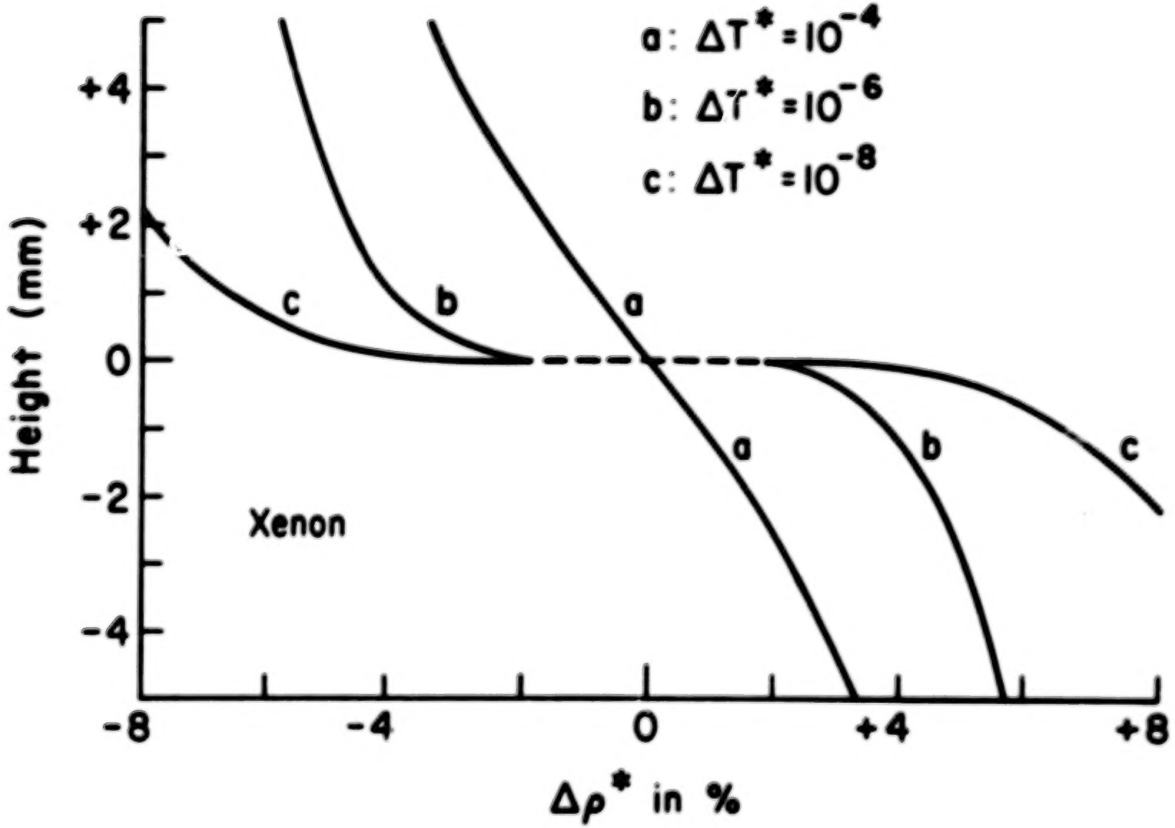

Figure 2. Calculated density profiles near the critical point of xenon in the earth's gravitational field. At the dashed part of the curves the density varies so rapidly that the assumption of local thermodynamic equilibrium is no longer valid.

Basically three different methods have been used to measure the local density as a function of height: floats, capacitance and refractive index as a function of height. As early as the beginning of the century Teichner [1904] used floats to indicate the existence of a density profile in CCl_4 near the critical point. Since the 1950's optical techniques have become increasingly popular. There exist principally two complementary optical methods, namely that in which the refractive index is measured as a function of height and that in which the refractive index gradient is measured as a function of height. The Lorentz-Lorenz relation is used to relate refractive index to density. The result of the first method is a density profile and that of the second method a compressibility profile. Capacitance measurements provide a fast and accurate method of determining fluid densities. Here the Clausius-Mosotti relationship is used to convert dielectric constants to densities. In a density profile experiment, a stack of capacitors is used to indicate the density at various levels.

For density or compressibility profile experiments to become quantitative, great care has to be taken to eliminate thermal gradients. Due to the strong divergence of the thermal expansion coefficients, even small temperature gradients yield appreciable contributions to the density profile. In view of the more awkward arrangements due to the need for windows, optical experiments have been more prone to thermal gradient errors than capacitance experiments. Moreover, as emphasized by Verschaffelt [1905], uncontrolled impurities may affect the observed density profile appreciably. Thus the earlier work (Lorentzen, 1953; Palmer, 1954; Schmidt and Traube, 1962; Schmidt,

1966), though pioneering, yielded conflicting results and only recently have profile studies become more quantitative. Straub [1967] improved the method of Schmidt and Traube for measuring the refractive index profile. A number of Russian investigators have used both the float method for measuring the density profile and the Schlieren method for measuring the refractive index gradient (Naumenko *et al.*, 1967; Artyukhovskaya *et al.*, 1971). Density profiles by measuring the dielectric constant as a function of height have been obtained by Weber [1970] and Thoen and Garland [1974]. The existence of concentration gradients near the critical mixing point of a binary liquid has also been confirmed experimentally (Lorentzen and Hansen, 1966; Blagoi *et al.*, 1970; Greer *et al.*, 1975; Giglio and Vendramini, 1975; Maisano *et al.*, 1976).

A very important experimental development was initiated by Wilcox and coworkers (Wilcox and Balzarini, 1968; Estler *et al.*, 1975) who perfected an optical interferometric method originally proposed by Gouy [1880] and who were able to reach a temperature stability to 20 microdegrees. A parallel beam of coherent light impinging on the cell will be deflected downward. Maximum deflection will occur at the level of maximum dn/dz, where n is the refractive index. Above and below this level, rays that experience the same deflection can be brou to interference after passage through a lens. The resulting interference pattern can be studied as a function of temperature; the location and order of the various maxima, counting from the maximally deflected beam upwards, contains all information necessary to obtain the equation of state. When combined with superior temperature control, this method has great potential. In practice, there are limitations to the number of decades in ΔT^* or $\Delta\rho^*$ where the method can be applied.

For the method to work away from the critical point it is necessary that the level of maximum dn/dz stays somewhere near the center of the cell. Since the locus of maximum dn/dz as a function of temperature probably does not coincide with a curve of precisely constant density, even the most careful filling of the cell cannot prevent the locus from moving out of the cell, limiting ΔT^* to values smaller than 10^{-4}. When the critical point is approached another cut-off is caused by gravity. When a band of strong refractive index gradients develops in the cell, the deflections of the rays become so large that they pass through fluid layers of widely varying density. This effect is proportional to the square of the thickness of the cell and provides a lower limit to all optical experiments. In practice, with cells a few mm thick, a range of $\Delta T^* < 10^{-5}$ is excluded, leaving a range of about one decade in temperature suitable for this technique (Moldover *et al.*, 1976).

When the density profile is measured using the capacitance method other limitations appear. First, dielectric constant experiments, unlike optical experiments, do not permit continuous sampling of the density as a function of height. Furthermore, dielectric constant experiments generally do not permit direct observation of the temperature of meniscus disappearance. Finally, the results can no longer be easily interpreted when the density variation between the plates of one capacitor exceeds the desired experimental accuracy.

The limitations imposed by gravity are very severe in calorimetric experiments. Since in calorimeters the bulk phase is heated, redistribution of matter in the cell yields an additional contribution to the specific heat which becomes appreciable at $\Delta T^* < 10^{-4}$

(Schmidt, 1971; Hohenberg and Barmatz, 1972). Since the specific heat anomaly is weak, background contributions are large everywhere except very close to the critical point. Thus the cut-off imposed by gravity restricts the precision with which the critical exponent α can be determined in earth-bound experiments.

In laser light scattering, measurements in the gravity-affected range can be carried out reliably if the intensity of the scattered light is measured as a function of the height in the cell (Alekhin *et al.*, 1969a,b; Chalyi and Alekhin, 1971; Golik *et al.*, 1969; Krupskii and Shimanskii, 1972; White and Maccabee, 1975). Gravity imposes limitations when the compressibility varies over the height of the scattering volume (Dobbs and Schmidt, 1973). However, the most severe limitations in the case of light scattering are not due to gravity but to multiple scattering and attenuation of the light beam.

Finally, there exists an intrinsic limit as to how closely the critical point can be approached in earth-bound experiments. Near the gas-liquid critical point a fluid exhibits large fluctuations in the density. The spatial extent of these fluctuations is characterized by a correlation length to be defined in Section 5.1. If the system were in true homogeneous thermodynamic equilibrium the compressibility and the correlation length would diverge at the critical point. However, the presence of a gravitational field prevents the fluctuations from growing indefinitely. At each level the system can be expected to be in local thermodynamic equilibrium, when the local fluid properties do not vary appreciably over the

distance of one correlation length. While the correlation length increases on approaching the critical point, the gravity induced density profile becomes more and more pronounced. Finally, a situation is reached where the fluid properties such as the compressibility and the correlation length vary non-negligibly over a height of the order of the correlation length. Then the assumption of local equilibrium ceases to be valid and the fluid properties themselves are modified by the gravitational field. These phenomena will be encountered at $|\Delta T^*| < 10^{-6}$; present-day experimental techniques are on the verge of entering this range.

In Table VI we present some estimates of the range where no accurate information is obtained in experiments conducted near the critical point of a fluid like xenon in the earth's gravitational field. For further details the reader is referred to a report by Moldover *et al.* [1976].

Table VI

Limitations Imposed by Gravity on Critical-Region Experiments[†]

Experiment	Property Measured	Characteristic Length	Nature of Limitation	Excluded Range $\rho = \rho_c$ ΔT^*	Excluded Range $T = T_c$ $\Delta\rho^*$
PVT	Density	Cell 1 cm High	Density gradient	6×10^{-4}	8×10^{-2}
Float densimeter	Density	Height of float 2.5 mm	Density gradient	2×10^{-4}	5×10^{-2}
Capacitance	Density	Spacing between plates 0.2 mm	Density gradient	2×10^{-5}	2×10^{-2}
Calorimetry	Heat capacity	Cell 1 cm high	Redistribution of matter	3.5×10^{-4}	6×10^{-2}
Refractive index gradient	Compressibility	Path in cell 3 mm	Curved path of beam in cell	1.5×10^{-5}	2×10^{-2}
Light scattering	Compressibility correlation length	Path in cell 3 mm	Turbidity	5×10^{-5}	3×10^{-2}
All	Any	Correlation length	Non local effects	1.5×10^{-6}	1.5×10^{-2}

[†]The estimates refer to xenon in the earth's gravitational field when the indicated property is to be measured within 1%. For details of obtaining these estimates see Moldover *et al.* [1976] and Hohenberg and Barmatz [1972].

III. Scaling Laws for Thermodynamic Properties of One-Component Fluids

3.1 Choice of Variables

In this section we describe the choice of variables we have made in scaling the thermodynamic properties of fluids, and the reasons for that choice. A critique of our choice of variables is postponed until Section 3.7.

As mentioned earlier, thermodynamics itself does not specify uniquely which set of variables is to be preferred in describing the critical behavior of fluids. The regularities found for the classical equations of state, e.g. the symmetry of the top of the coexistence curve, are present for any choice of variables, such as $\rho(T)$ or $V(T)$ or even $\rho(P)$, in which we care to describe the coexistence curve. On the other hand, in the lattice gas one system of variables is to be preferred distinctly. The lattice gas has perfect antisymmetry with respect to the critical isochore when μ is considered as a function of ρ, while this symmetry property is lacking in any other set of variables. The analyticity of μ on the critical isochore gives the possibility of scaling to a higher order in ΔT^* than is possible for the classical equations. Thus if the assumption of scaling is to be tested on numerical data for the lattice gas, it is clearly advisable to consider $\mu(\rho,T)$ rather than $P(V,T)$. The first choice of variables guarantees a much larger range of asymptotic validity of scaling and the possibility of scaling the specific heat C_V.

For real fluids we do not know *a priori* which variables are to be preferred in describing critical behavior and the choice we have made

is based on empirical considerations of symmetry (Tisza and Chase, 1965; Vicentini-Missoni et al., 1969a; Levelt Sengers, 1970). The shape of the coexistence curve can be studied by plotting either the coexisting volumes or the coexisting densities as a function of temperature as shown for argon in Fig. 3. In terms of ρ and T the coexistence curve shows much more symmetry than in terms of V and T. In the lattice gas the coexistence curve $\rho_{cxc}(T)$ would be perfectly symmetric. In a real fluid, like argon, the lack of complete symmetry is evident from the locus of average coexisting densities which is approximately a straight line, the "rectilinear diameter" but which does not coincide with the critical isochore $\rho = \rho_c$.

In the one-phase region of real fluids we notice a clear preference for a description in terms of $\mu(\rho,T)$ rather than $P(\rho,T)$. In Fig. 4 P(V)-isotherms and $\mu(\rho)$-isotherms are shown for argon; in contrast to the P(V)-isotherms, the $\mu(\rho)$-isotherms are remarkably antisymmetric with respect to ρ_c.

The analytic behavior of pressure and chemical potential on the critical isochore appears also to be different. In Fig. 5 the two-phase specific heat C_V^*/T^* of steam (Amirkhanov and Kerimov, 1963) is plotted as a function of $\Delta\rho^*$. According to the Yang-Yang relation (2.34) the slope of the tie lines equals $d^2\mu/dT^2$ and it does not vary much in a temperature range of 10%. The intercepts of the tie lines equal d^2P/dT^2 and they show an appreciable increase on approaching T_c. In the lattice gas $d^2\mu/dT^2$ would be constant, while d^2P/dT^2 would diverge weakly like C_V. Hence, the asymptotic symmetry features of real fluids are reminiscent of those of the lattice gas.

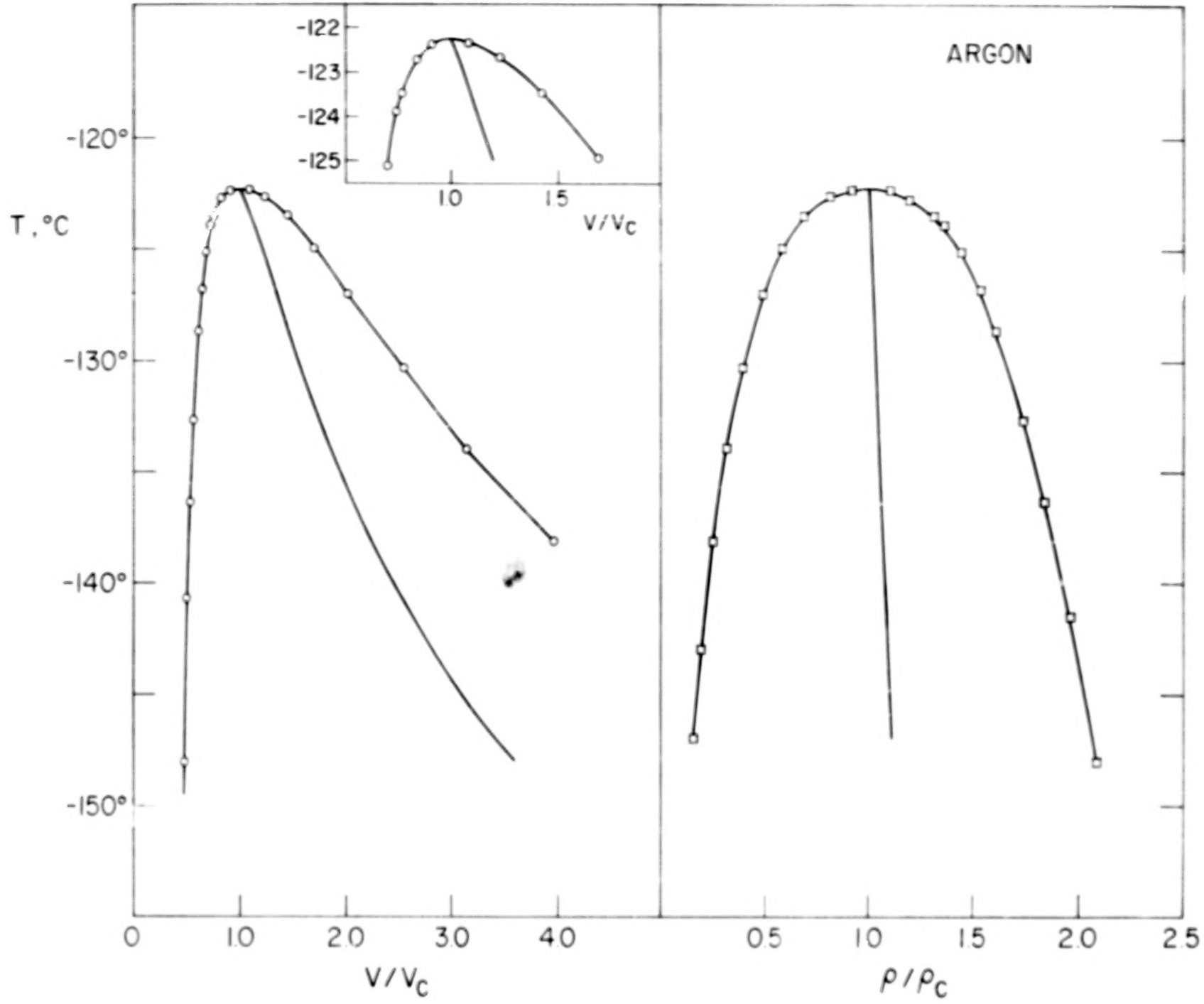

Figure 3. The coexistence curve of argon in terms of volume and temperature and in terms of density and temperature.

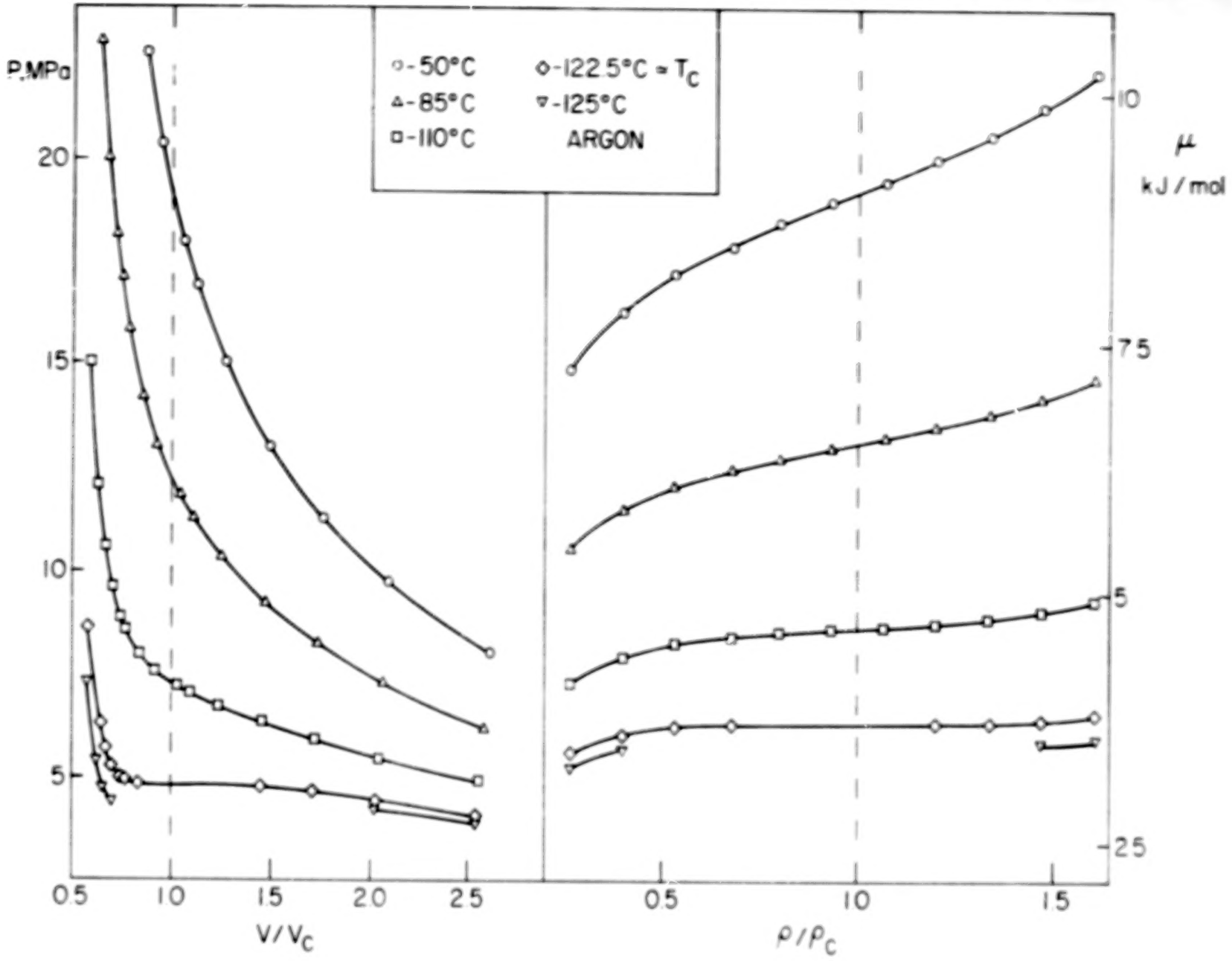

Figure 4. P(V) isotherms and μ(ρ) isotherms of argon in the critical region. In contrast to the P(V) isotherms, the μ(ρ) isotherms are nearly antisymmetric with respect to ρ_c.

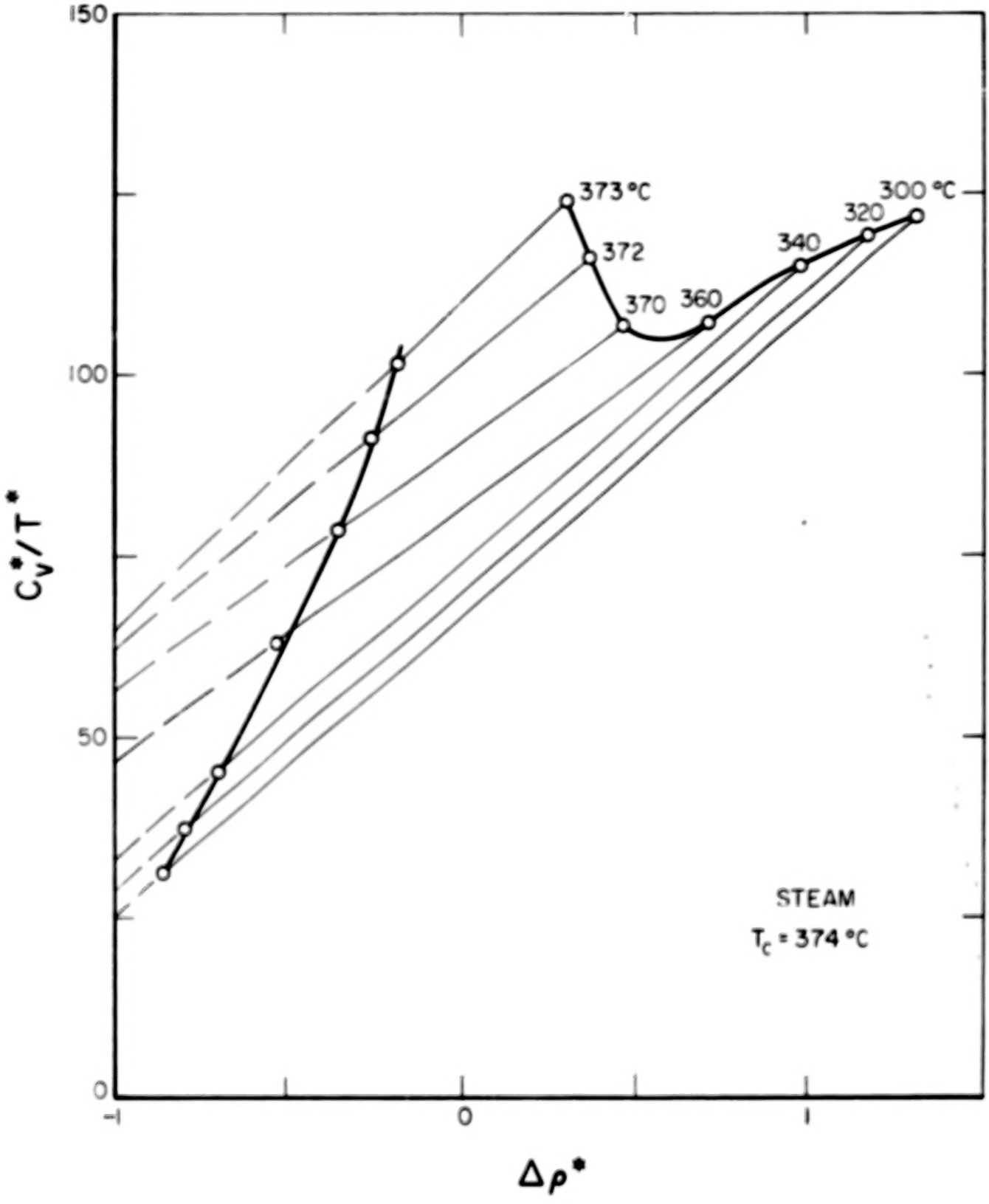

Figure 5. The two-phase specific heat C_v^*/T^* of steam as a function of $\Delta\rho^*$. The slope of the tie lines equals $d^2\mu^*/dT^{*2}$ and the intercept equals d^2P^*/dT^{*2}.

Based on these arguments we choose as independent variables the lattice-gas variables $\Delta\rho^*$ and ΔT^* and as dependent variable for the equation of state we take $\Delta\mu^* = \mu^*(\rho^*,T^*) - \mu^*(\rho_c{}^*,T^*)$. The Helmholtz free energy density is written in the form

$$A^* = A_o{}^*(T^*) + \rho^*\mu^*(\rho_c{}^*,T^*) + A^*_{sing}(\Delta\rho^*,\Delta T^*) \tag{3.1}$$

such that $(\partial A^*_{sing}/\partial\Delta\rho^*)_T = \Delta\mu^*$. $A_o{}^*(T^*)$ is an analytic background term depending on temperature, while A^*_{sing} is the singular part representing the anomalous thermodynamic behavior near the critical point. It is assumed that A^*_{sing} is symmetric and $\Delta\mu^*$ antisymmetric in $\Delta\rho^*$

$$\begin{aligned} A^*_{sing}(-\Delta\rho^*, T^*) &= A^*_{sing}(\Delta\rho^*,\Delta T^*) \\ \Delta\mu^*(-\Delta\rho^*, T^*) &= -\Delta\mu^*(\Delta\rho^*,\Delta T^*) \end{aligned} \tag{3.2}$$

The range over which these symmetry relations hold depends on the nature of the fluid and the precision of the experimental data: that is, the more precise the data, the sooner they will reveal departures from symmetry. For many available equation of state data a rough guideline for the range of symmetry is $\Delta\rho^* = \pm 0.25$. The symmetry relations (3.2) ignore the difference between the critical isochore and the rectilinear diameter when applied below the critical temperature. The coexistence dome of most fluids is so wide that a state with $\Delta\rho^* = \pm 0.25$ is reached within $|\Delta T^*| = 3 \times 10^{-3}$, in which range the departure from the rectilinear diameter from ρ_c is very small. Modifications in the choice of variables that may be needed to incorporate departures from perfect symmetry around ρ_c will be discussed in Section 3.7.

3.2 Homogeneity Postulate

It has been observed experimentally that the singular parts of various thermodynamic properties follow a power law when the critical point is approached along the critical isochore $\Delta\rho^* = 0$, the critical isotherm $\Delta T^* = 0$ and along the coexistence curve $\Delta\rho^*/|\Delta T^*|^\beta = \pm B$ (Heller, 1967). Hence, in analogy with (2.45) and (2.46), one is led to assume that the singular parts of these thermodynamic functions are generalized homogeneous functions of $\Delta\rho^*$ and ΔT^*. This homogeneity postulate was first formulated by Widom [1965a] for the singular part of the chemical potential. Here we adopt the formulation of Griffiths [1967] assuming that the singular part A^*_{sing} of the Helmholtz free energy density in the one-phase region is a generalized homogeneous function of its characteristic variables $\Delta\rho^*$ and ΔT^*

$$A^*_{sing}(\lambda^{a_\rho}\Delta\rho^*, \lambda^{a_T}\Delta T^*) = \lambda A^*_{sing}(\Delta\rho^*, \Delta T^*) \ . \tag{3.3}$$

This hypothesis of homogeneity finds support in the known properties of the lattice gas, confirmed by the renormalization group theory. However, since the lattice gas is a highly artificial model of a fluid, the assumption of homogeneity and the choice of variables for real fluids remain empirical postulates which may have to be modified.

The homogeneity property (3.3) for A^*_{sing} implies that the chemical potential difference $\Delta\mu^*$, the isothermal compressibility $\gamma_T^* = (\partial\mu^*/\partial\rho^*)_T$ and the singular contribution to the entropy $S^*_{sing} = -(\partial A^*_{sing}/\partial T^*)_\rho$ and specific heat $C^*_{V,sing}/T^* = -(\partial^2 A^*_{sing}/\partial T^{*2})_\rho$ are also generalized homogeneous functions of $\Delta\rho^*$ and ΔT^*. After

differentiating (3.3) and redefining the parameter λ appropriately one obtains (Hankey and Stanley, 1972; Levelt Sengers, 1975)

$$\Delta\mu^*(\lambda^{a_\rho/(1-a_\rho)}\Delta\rho^*, \lambda^{a_T/(1-a_\rho)}\Delta T^*) = \lambda\Delta\mu^*(\Delta\rho^*, \Delta T^*), \tag{3.4a}$$

$$\chi_T^{*-1}(\lambda^{a_\rho/(1-2a_\rho)}\Delta\rho^*, \lambda^{a_T/(1-2a_\rho)}\Delta T^*) = \lambda\chi_T^{*-1}(\Delta\rho^*, \Delta T^*), \tag{3.4b}$$

$$S^*_{sing}(\lambda^{a_\rho/(1-a_T)}\Delta\rho^*, \lambda^{a_T/(1-a_T)}\Delta T^*) = \lambda S^*_{sing}(\Delta\rho^*, \Delta T^*), \tag{3.4c}$$

$$\frac{C^*_{V,sing}}{T^*}(\lambda^{a_\rho/(1-2a_T)}\Delta\rho^*, \lambda^{a_T/(1-2a_T)}\Delta T^*) = \lambda\frac{C^*_{V,sing}}{T^*}(\Delta\rho^*, \Delta T^*) . \tag{3.4d}$$

Along the critical isochore $\Delta\rho^* = 0$ and along the critical isotherm $\Delta T^* = 0$ these thermodynamic properties will vary according to power laws analogous to (2.46). In particular

$$\chi^{*-1}(0, \Delta T^*) = \chi^{*-1}(0,1)(\Delta T^*)^{(1-2a_\rho)/a_T} \qquad (\Delta T^* \geq 0) ,$$

$$\frac{C^*_{V,sing}}{T^*}(0, T^*) = \frac{C^*_{V,sing}}{T^*}(0,1)(\Delta T^*)^{(1-2a_T)/a_T} \qquad (\Delta T^* \geq 0) ,$$

$$\Delta\mu^*(\Delta\rho^*, 0) = \pm\Delta\mu^*(1,0)|\Delta\rho^*|^{(1-a_\rho)/a_\rho} .$$

For the two coexisting phases below the critical temperature $\Delta\mu^* = 0$, while $\Delta\rho^*_{cxc} \neq 0$. From the homogeneity assumption (3.4a) it follows that at coexistence $\Delta\mu^*(|\Delta T^*|^{-a_\rho/a_T}\Delta\rho^*, -1) = 0$, so that

$$|\Delta T^*|^{-a_\rho/a_T}\Delta\rho^*_{cxc} = \pm B .$$

where B is constant. The power law behavior of the compressibility and the specific heat along the coexistence curve $\Delta\rho^*/|\Delta T^*|^{a_\rho/a_T} = \pm B$ follows from (3.4b) and (3.4d) in analogy with (2.45)

$$\chi^{*-1}(\Delta\rho^*_{cxc},\Delta T^*) = \chi^{*-1}(B,-1)\,|\Delta T^*|^{(1-2a_\rho)/a_T} ,$$

$$\frac{C^*_{V,sing}}{T^*}(\Delta\rho^*_{cxc},\Delta T^*) = \frac{C^*_{V,sing}}{T^*}(B,-1)\,|\Delta T^*|^{(1-2a_T)/a_T} .$$

The specific heat anomaly in the two-phase region is obtained by observing that the singular part A_s^* of the free energy inside the two-phase region is independent of the density and equal to its value at the phase boundary: $A^*_{sing,II} = A^*_{sing}(\Delta\rho^*_{cxc},\Delta T^*) = A^*_{sing}(B,-1)\,|\Delta T^*|^{1/a_T}$. Differentiation yields for the specific heat anomaly in the two-phase region

$$\left(\frac{C^*_{V,sing}}{T^*}\right)_{II} = -\frac{1}{a_T}\left(\frac{1}{a_T}-1\right)A^*_{sing}(B,-1)\,|\Delta T^*|^{(1-2a_T)/a_T} .$$

We thus have recovered the thermodynamic power laws introduced in Table I with

$$\alpha = \alpha' = \alpha'' = (2a_T-1)/a_T,\ \beta = a_\rho/a_T ,$$
$$\gamma = \gamma' = (1-2a_\rho)/a_T,\ \delta = (1-a_\rho)/a_\rho , \qquad (3.5)$$

so that

$$a_\rho = \frac{1}{\delta+1} = \frac{\beta}{2-\alpha},\quad a_T = \frac{1}{\beta(\delta+1)} = \frac{1}{2-\alpha} . \qquad (3.6)$$

The thermodynamic critical exponents satisfy the relations (2.5) and all power laws are determined by two independent exponents only.

3.3 Thermodynamic Scaling Laws

The homogeneity postulate (3.3) implies in analogy with (2.44) that the symmetric part of the Helmholtz free energy density satisfies a scaling law of the form

$$\frac{A^*_{sing}(\Delta\rho^*,\Delta T^*)}{|\Delta\rho^*|^{\delta+1}} = A^*_{sing}(1,x) \ , \tag{3.7}$$

where the scaling variable x is defined as

$$x = \Delta T^*/|\Delta\rho^*|^{1/\beta} \ . \tag{3.8}$$

We find it convenient to write $A^*_{sing}(1,x) = Da(x/x_o)$, where D is the amplitude of the power law $\Delta\mu^* = D(\Delta\rho^*)|\Delta\rho^*|^{\delta-1}$ for the critical isotherm and where x_o is related to the amplitude B of the power law $\Delta\rho^*_{cxc} = \pm B|\Delta T^*|^{\beta}$ for the coexistence curve by

$$x_o = B^{-1/\beta} \ . \tag{3.9}$$

Thus the Helmholtz free energy density (3.1) can be written in scaled form as

$$A^* = A_o^*(T^*) + \rho^*\mu^*(\rho_c^*,T^*) + |\Delta\rho^*|^{\delta+1}Da(x/x_o) \ . \tag{3.10}$$

For the chemical potential difference $\Delta\mu^* = (\partial A^*_{sing}/\partial\Delta\rho^*)_T$ we obtain the scaling law

$$\Delta\mu^* = \Delta\rho^*|\Delta\rho^*|^{\delta-1}Dh(x/x_o) \ , \tag{3.11}$$

where the functions $a(x/x_o)$ and $h(x/x_o)$ are related by the differential equation (Griffiths, 1967; Levelt Sengers *et al.*, 1976)

$$\beta h(w) = -wa'(w) + \beta(\delta+1)a(w) \ , \tag{3.12}$$

with $a'(w) = da/dw$. Curves of constant x in the $\Delta\rho^* - \Delta T^*$ plane are schematically indicated in Fig. 6. The curve $x = -x_o$ is the coexistence curve, the curve $x = 0$ is the critical isotherm and the curve $x = \infty$ is the critical isochore. The function $h(x/x_o)$ is normalized such that at the critical isotherm $h(0) = 1$. From (3.10) and (3.11) one can deduce scaled expressions for all thermodynamic properties in terms of $a(x/x_o)$ and $h(x/x_o)$; some of these expressions are given in Table VII.

When the experimental values of the ratios $\Delta\mu^*/(\Delta\rho^*)|\Delta\rho^*|^{\delta-1}$ are plotted as a function of the scaling variable x/x_o, then the scaling law (3.11) predicts that different isotherms should all collapse onto one single curve. An example of such a scaled plot is presented in Fig. 7 for ^{4}He as deduced from the data of Roach (1968) assuming $\beta = 0.355$ and $\gamma = 1.19$ (Levelt Sengers *et al.*, 1976).

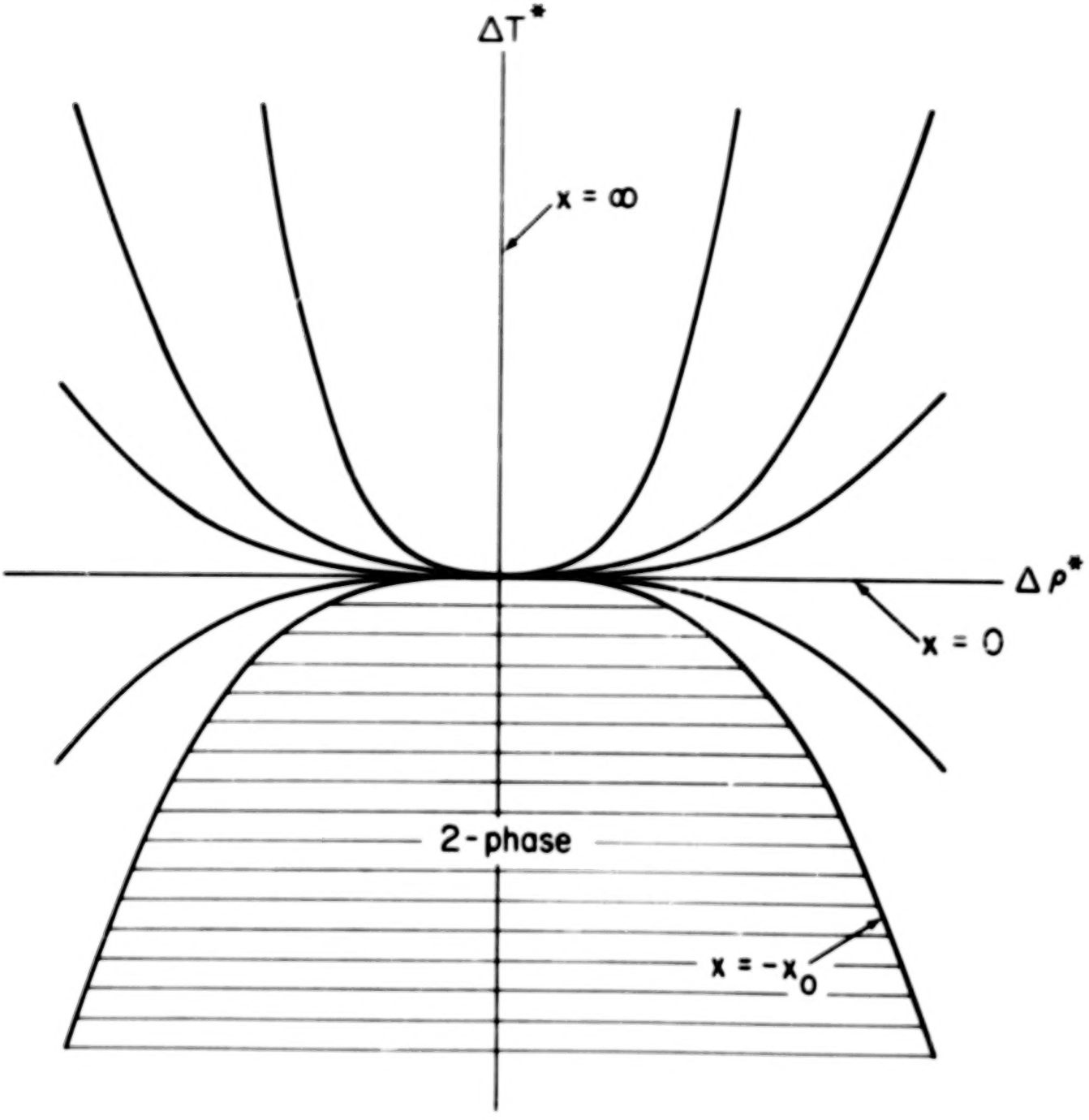

Figure 6. Curves of constant x in the $\Delta\rho^* - \Delta T^*$ plane.

Table VII

Scaled Expressions for Thermodynamic Functions

Chemical Potential

$$\mu^* = \mu^*(\rho_c^*, T^*) + \Delta\rho^* |\Delta\rho^*|^{\delta-1} D h\left(\frac{x}{x_0}\right)$$

Compressibility

$$\chi_T^{*-1} = (\rho^{*2} K_T^*)^{-1} = |\Delta\rho^*|^{\delta-1} D\left\{\delta h\left(\frac{x}{x_0}\right) - \frac{x}{\beta x_0} h'\left(\frac{x}{x_0}\right)\right\}$$

Helmholtz Free Energy

$$A^* = A_0^*(T^*) + \rho^* \mu^*(\rho_c^*, T^*) + |\Delta\rho^*|^{\delta+1} D a\left(\frac{x}{x_0}\right)$$

Pressure

$$P^* = -A_0^*(T^*) + D\left[\Delta\rho^* |\Delta\rho^*|^{\delta-1} h\left(\frac{x}{x_0}\right) + |\Delta\rho^*|^{\delta+1}\left\{h\left(\frac{x}{x_0}\right) - a\left(\frac{x}{x_0}\right)\right\}\right]$$

Entropy

$$-S^* = \frac{dA_0^*(T^*)}{dT^*} + \rho^* \frac{d\mu^*(\rho_c^*, T^*)}{dT^*} + |\Delta\rho^*|^{(1-\alpha)/\beta} \frac{D}{x_0} a'\left(\frac{x}{x_0}\right)$$

Heat Capacity

$$-\frac{C_V^*}{T^*} = \frac{d^2 A_0^*(T^*)}{dT^{*2}} + \rho^* \frac{d^2 \mu^*(\rho_c^*, T^*)}{dT^{*2}} + |\Delta\rho^*|^{-\alpha/\beta} \frac{D}{x_0^2} a''\left(\frac{x}{x_0}\right)$$

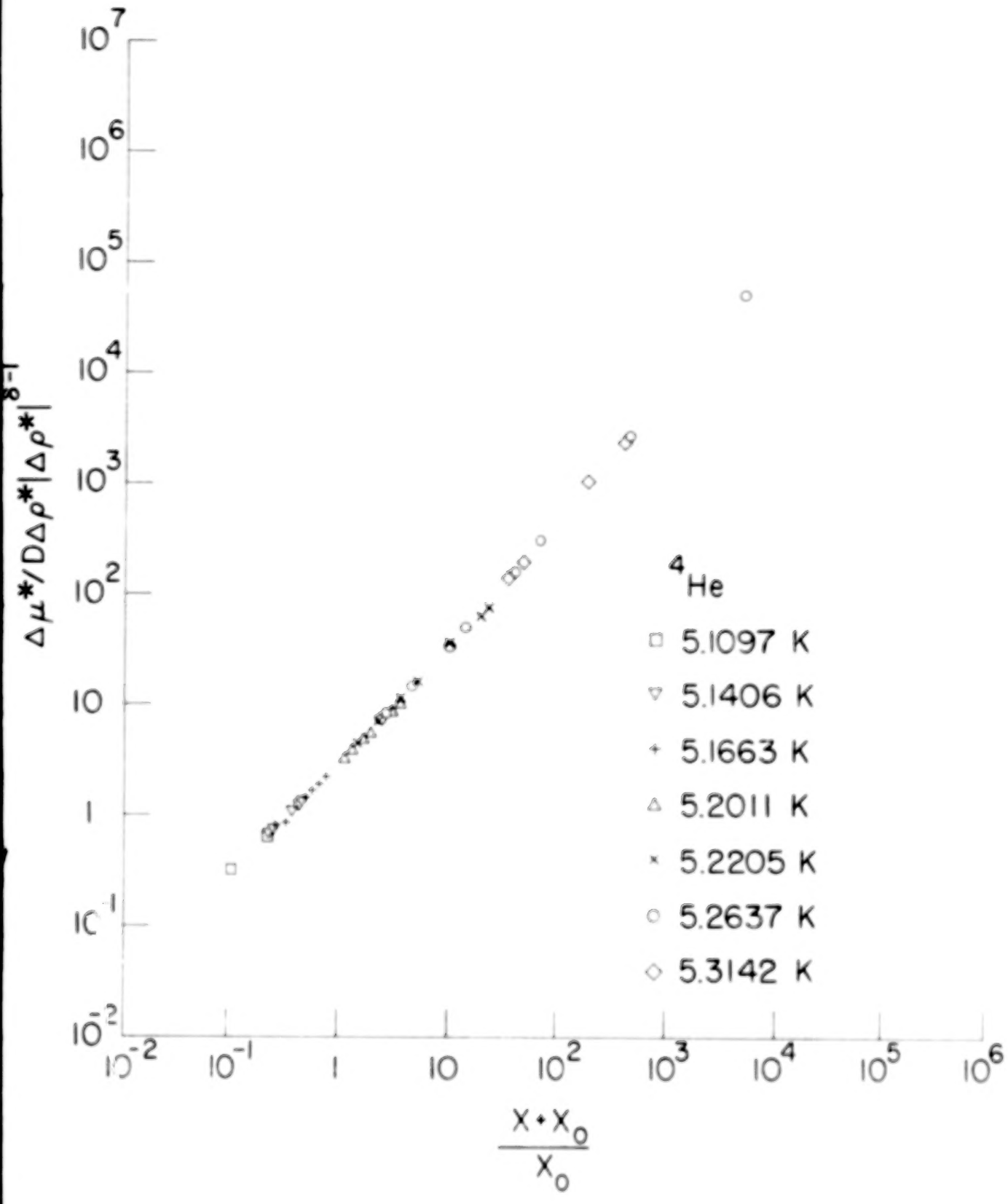

Figure 7. Scaled chemical potential data for ^{4}He as a function of $(x+x_o)/x_o$. Reduction parameters are taken from Table X.

3.4 Scaled Equations of State

The scaling laws are a conjecture regarding the asymptotic behavior of the thermodynamic properties in the vicinity of the critical point. When the scaling laws are applied in a finite range of densities and temperatures the results may be affected by the presence of less singular correction terms not taken into account. As a consequence the actual range of the validity of the scaling laws will depend on the precision of the experimental data. The more precise the data, the sooner deviations from asymptotic scaling behavior will be detected.

We shall first discuss a number of results deduced from an analysis of equation of state data in the range $5 \times 10^{-4} \leq |\Delta T^*| \leq 3 \times 10^{-2}$ not significantly affected by gravity. In Section 3.6 we shall then comment on some recent density gradient profile measurements obtained at temperatures $|\Delta T^*| < 10^{-4}$ and indicate how they affect our understanding of the thermodynamic behavior of real fluids near the critical point.

In order to make a quantitative analysis of the experimental thermodynamic data one needs an expression for the scaling functions h(w) or a(w), where $w = x/x_o$. In the absence of an *a priori* theoretical expression for fluids one has formulated approximate expressions of an empirical nature. The choices for the function h(w) are restricted by a number of conditions formulated by Griffiths [1967]. Some of these conditions arise from the requirements of thermodynamic stability. Mechanical stability requires the compressibility to be positive so that

$$\beta\delta h(w) \geq wh'(w) . \qquad (3.13)$$

Thermal stability requires the specific heat to be positive so that (Vicentini-Missoni, 1971)

$$a''(w) \leq 0 . \qquad (3.14)$$

Additional conditions are imposed on h(w) by the assumption that $\mu(\rho,T)$ is an analytic function throughout the one-phase region with the exception of the critical point and perhaps the phase boundary. Thus h(w) should be analytic in the range $-1 < w < \infty$; specifically for small values of w, h(w) should have an expansion of the form

$$h(w) = 1 + \sum_{n=1}^{\infty} h_n w^n . \qquad (3.15)$$

Analyticity of μ at large w implies that h(w) can be expanded around $w = \infty$ as

$$h(w) = \sum_{n=1}^{\infty} \eta_n w^{\beta(\delta+1-2n)} . \qquad (3.16)$$

It has not been possible to formulate a closed form for h(w) that satisfies all these conditions. Vicentini-Missoni, Levelt Sengers and Green [1969a,b] proposed an approximate expression to which we refer as the MLSG equation (NBS equation in the original literature)

$$h(w) = (1+w)\left[\frac{1+E_2(1+w)^{2\beta}}{1+E_2}\right]^{(\gamma-1)/2\beta} , \qquad (3.17)$$

where E_2 is an additional adjustable parameter. In this approximation the equation of state (3.11) reads

$$\Delta\mu^* = \Delta\rho^* |\Delta\rho^*|^{\delta-1} E_1 \left(1 + \frac{x}{x_o}\right) \left[1 + E_2 \left(1 + \frac{x}{x_o}\right)^{2\beta}\right]^{(\gamma-1)/2\beta} , \qquad (3.18)$$

with

$$E_1 = \frac{D}{(1+E_2)^{(\gamma-1)/2\beta}} . \qquad (3.19)$$

The MLSG equation has been used to represent experimental equation of state data for a variety of fluids (Vicentini *et al.*, 1969a,b; Wallace and Meyer, 1970; Levelt Sengers *et al.*, 1976; Gulari and Pings, 1973). As an example of the quality of the fit we show in Fig. 8 a deviation plot when the chemical potential data deduced from the P-V-T data of Rivkin *et al.* [1962, 1963, 1964, 1966] for steam are fitted to the MLSG equation (Levelt Sengers *et al.*, 1976).

The MLSG equation has the advantage that it expresses the equation of state in terms of the primary variables $\Delta\rho^*$ and ΔT^*. However, it has two disadvantages. Firstly, while the equation does satisfy the analyticity requirement for small values of w, it reproduces correctly only the first two terms of the series expansion (3.16) for large values of w. Secondly, the equation cannot be integrated analytically to yield a closed form for the function a(w) (Schmidt, 1971; Lentini and Vicentini-Missoni, 1973). Hence, the equation does not provide a satisfactory basis for developing a fundamental equation and it can only be fitted to experimental P-V-T data after they have been integrated numerically to yield chemical potential data.

The two problems can be overcome by using parametric equations introduced by Schofield [1969] and Josephson [1969]. This formulation

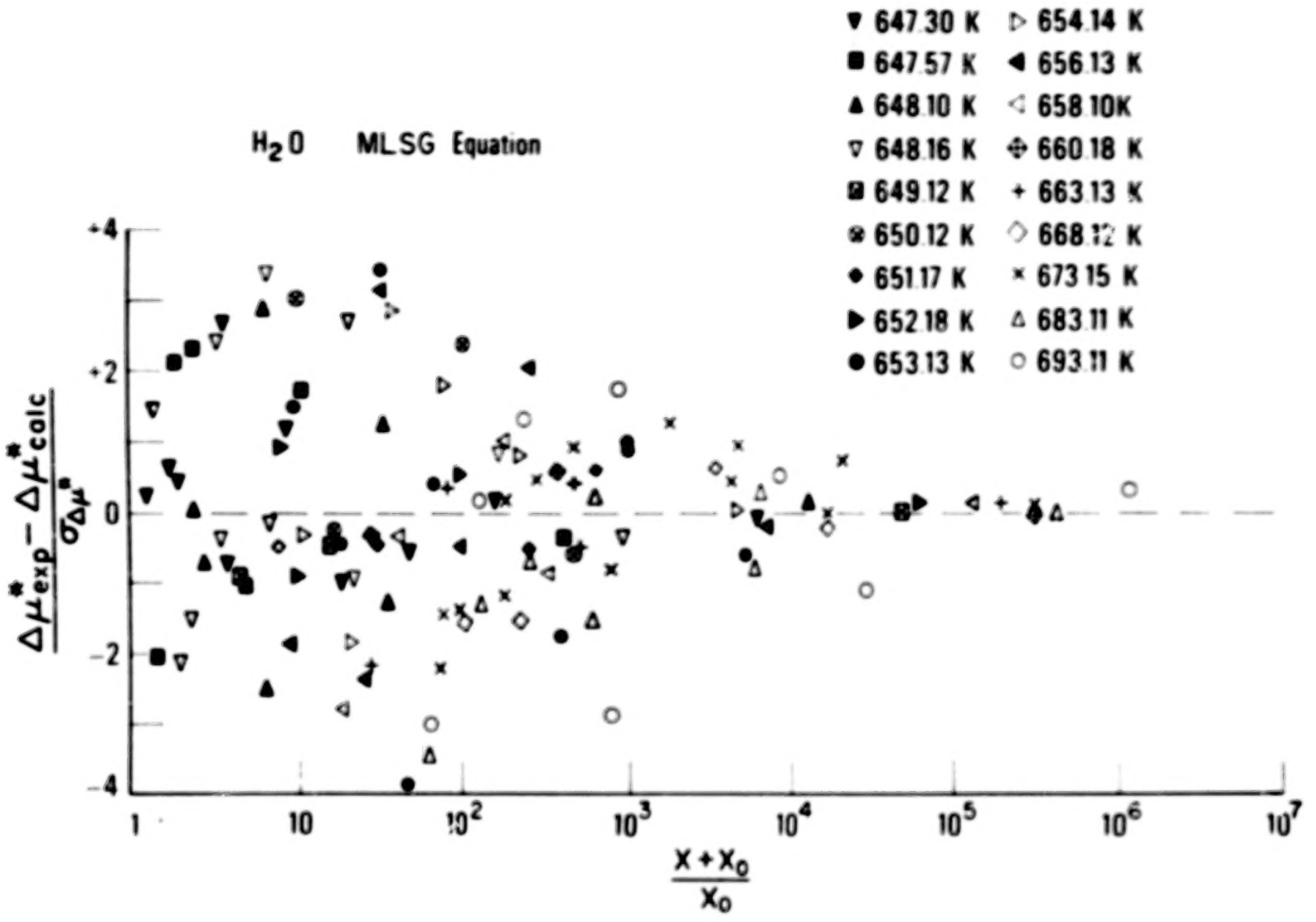

Figure 8. Plot of normalized deviations $(\Delta\mu^*_{exp} - \Delta\mu^*_{calc})/\sigma_{\Delta\mu^*}$ as a function of $(x+x_0)/x_0$ for H_2O (MLSG equation). $\sigma_{\Delta\mu^*}$ is the estimated experimental uncertainty; $\Delta\mu^*_{calc}$ is calculated from the MLSG equation with parameters ρ_c = 322.2 kg/m^3, T_c = 647.05 K, β = 0.350, δ = 4.50, x_0 = 0.100, E_1 = 1.215, E_2 = 0.372 (Levelt Sengers *et al.*, 1976).

entails a transformation from the physical variables ΔT^* and $\Delta\rho^*$, into two parametric variables, r and θ. The variable r is meant, in some sense, to describe how closely the critical point is approached and the variable θ a "location on a contour of constant r." All anomalies are then incorporated by the power laws in the r-dependence, while the θ-dependence is kept analytic.

The manner in which the thermodynamic variables are expressed in terms of r and θ is not unique (Fisher, 1971). The constraints that the scaling laws are preserved are met by the following choice

$$\begin{aligned} \Delta T^* &= rT(\theta) \quad , \\ \Delta\rho^* &= r^{\beta} M(\theta) \quad , \\ \Delta\mu^* &= r^{\beta\delta} H(\theta) \quad . \end{aligned} \tag{3.20}$$

On constructing the ratios $\Delta\mu^*/(\Delta\rho^*)|\Delta\rho^*|^{\delta-1}$ and $x = \Delta T^*/|\Delta\rho^*|^{1/\beta}$ one sees immediately that both ratios depend on θ alone, so that the scaling law (3.11) is implied by the parametric representation (3.20). The parameter θ can be chosen to span the range -1 to +1, such that it equals zero on the critical isochore and ± 1 on the coexistence boundary, as indicated schematically in Fig. 9. Choices compatible with the assumed lowest order symmetry are those for which $T(\theta)$ is a symmetric function of θ and $M(\theta)$ and $H(\theta)$ are antisymmetric functions of θ. The two most popular choices compatible with these requirements are either the *linear* model (Schofield, 1969) for which

$$\begin{aligned} T(\theta) &= 1 - b_1{}^2\theta^2 \quad , \\ M(\theta) &= k_1\theta \quad , \\ H(\theta) &= a_1\theta(1-\theta^2) , \end{aligned} \tag{3.21}$$

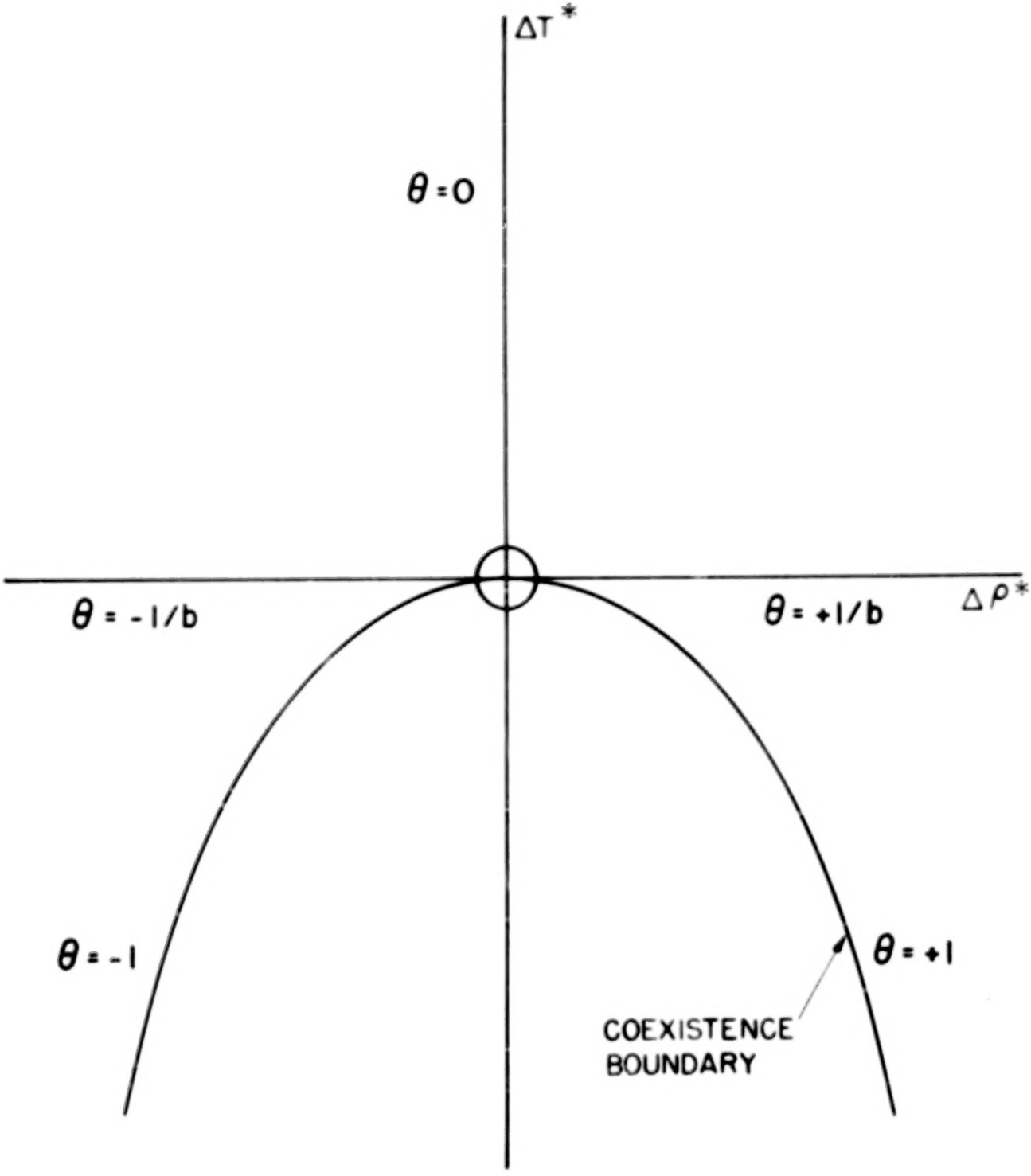

Figure 9. The variable θ in the parametric equations of state.

or the *cubic model* (Ho and Litster, 1970) for which

$$T(\theta) = 1-k_2^2\theta^2 \quad ,$$
$$M(\theta) = k_2\theta(1+c\theta) \quad , \qquad (3.22)$$
$$H(\theta) = a_2\theta(1-\theta^2) \quad ,$$

The linear model contains three constants k_1, a_1, b_1 and the cubic model four constants k_2, a_2, b_2, c which have to be determined. Slightly more elaborate parametric equations have been considered by Kierstead [1973] and Estler *et al.* [1975]. The relationships between the constants of the scaled equations presented here and the amplitudes of the thermodynamic power laws introduced in Table I are given in Table VIII.

Both the linear model and the cubic model can be integrated analytically to yield the Helmholtz free energy density and, hence, the other thermodynamic functions (Hohenberg and Barmatz, 1972). The parametric representations for various thermodynamic properties are given in Table IX. For reasons to be discussed in the subsequent section, one often uses restricted versions of these parametric equations in which the constant b_1 of the linear model or the constants b_2 and c of the cubic model are fixed by the conditions presented at the bottom of Table IX.

Various authors have analyzed experimental data in terms of the linear model (Anisimov *et al.*, 1974; Ho and Litster, 1969; Hohenberg and Barmatz, 1972; Huang and Ho, 1973; Levelt Sengers *et al.*, 1974, 1976; Murphy *et al.*, 1973, 1975; Thoen and Garland, 1974; White and Maccabee, 1975). It turns out that the linear model, as well as the cubic model (Huang and Ho, 1973; Murphy, 1975), yields a satisfactory representation

Table VIII

Amplitudes of Power Laws

MLSG Equation

$$B = x_0^{-\beta}$$

$$D = E_1(1+E_2)^{(\gamma-1)/2\beta}$$

$$\Gamma = x_0^{\gamma}/E_1E_2^{(\gamma-1)/2\beta}$$

$$\Gamma' = \beta x_0^{\gamma}/E_1$$

Parametric Equations[+]

$$B = k(1+c)/(b^2-1)^{\beta}$$

$$D = a(b^2-1)b^{3(\delta-1)}/k^{\delta}(b^2+c)^{\delta}$$

$$\Gamma = k/a$$

$$\Gamma' = (b^2-1)^{\gamma-1}[1-b^2\{1-2\beta)-c\{b^2(3-2\beta)-3\}]k/2a$$

$$A^{+} = -ak(2-\alpha)(1-\alpha)\alpha f_0$$

$$A_1^{-} = ak\alpha(b^2-1)^{\alpha}\{\frac{(1-\alpha)(1+3c)(s_0+s_2+s_4)-2\beta(1+c)(s_2+2s_4)}{1-b^2(1-2\beta)-c\{b^2(3-2\beta)-3\}}\}$$

$$A_{II}^{-} = -ak(2-\alpha)(1-\alpha)\alpha(f_0+f_2+f_4+f_6)/(b^2-1)^{2-\alpha}$$

[+]For definition of f_i (i = 0,2,4,6) and s_j (j = 0,2,4) see Table IX.

Table IX

PARAMETRIC REPRESENTATION OF THERMODYNAMIC FUNCTIONS

(Linear model: $c = 0$; cubic model: $c \neq 0$)

Variables	$\Delta T^* = r(1-b^2\theta^2)$ $\Delta\rho^* = r^{\beta}k\theta(1+c\theta^2)$
Chemical Potential	$\mu^* = \mu^*(\rho_c^*, T^*) + r^{\beta\delta}a\theta(1-\theta^2)$
Compressibility	$\left(\frac{\partial\rho^*}{\partial\mu^*}\right)_T = \chi_T^* = r^{-\gamma}\frac{k}{a}\frac{1-(b^2-2\beta b^2-3c)\theta^2 - (3-2\beta)b^2c\theta^4}{1-(b^2-2\beta\delta b^2+3)\theta^2 - (2\beta\delta-3)b^2\theta^4}$
Helmholtz free energy	$A^* = A_o^*(T^*) + \rho^*\mu^*(\rho_c^*, T^*) + r^{2-\alpha}akf(\theta)$
where	$f(\theta) = f_0 + f_2\theta^2 + f_4\theta^4 + f_6\theta^6$
	$f_0 = -\frac{\beta(\delta-3)-b^2\alpha\gamma}{2b^4(2-\alpha)(1-\alpha)\alpha} + \frac{c\{b^2(1+\alpha)(3\gamma+2\beta)-6\gamma\}}{2b^6(2-\alpha)(1-\alpha)\alpha(1+\alpha)}$
	$f_2 = +\frac{\beta(\delta-3)-b^2\alpha(1-2\beta)}{2b^2(1-\alpha)\alpha} - \frac{c\{b^2(1+\alpha)(3\gamma+2\beta)-6\gamma\}}{2b^4(1-\alpha)\alpha(1+\alpha)}$
	$f_4 = -\frac{1-2\beta}{2\alpha} + \frac{c\{b^2(1+\alpha)(3-2\beta)-3\gamma\}}{2b^2\alpha(1+\alpha)}$
	$f_6 = -\frac{(3-2\beta)}{2(1+\alpha)}c$
Pressure	$P^* = -A_o^*(T^*) + r^{\beta\delta}a\theta(1-\theta^2)$ $+ r^{2-\alpha}ak\{\theta^2(1-\theta^2)(1+c\theta^2) - f(\theta)\}$
Entropy	$S^* = -\frac{dA_o^*(T^*)}{dT^*} - \rho^*\frac{d\mu^*(\rho_c^*, T^*)}{dT^*} + r^{1-\alpha}aks(\theta)$
where	$s(\theta) = s_0 + s_2\theta^2 + s_4\theta^4$
	$s_0 = -(2-\alpha)f_0$, $s_2 = -(2-\alpha)b^2(1-2\beta)f_0 - \gamma f_2$, $s_4 = -3\gamma c/2b^2(1+\alpha)$

Table IX (continued)

Pressure Coefficient	$\left(\frac{\partial P^*}{\partial T^*}\right)_T = -\frac{dA_o^*(T^*)}{dT^*} + r^{1-\alpha} a_{ks}(\theta) \cdot + (1+\Delta\rho^*) r^{\beta\delta-1} a_{\beta\theta} \left\{ \frac{\delta(1-\theta^2)(1+3c\theta^2) - (1-3\theta^2)(1+c\theta^2)}{1-(b^2-2\beta b^2-3c)\theta^2 - (3-2\beta)b^2c\theta^4} \right\}$
Heat Capacity	$\frac{C_V^*}{T^*} = -\frac{d^2 A_o^*(T^*)}{dT^{*2}} - \rho^* \frac{d^2 \mu^*(\rho_c^*, T^*)}{dT^{*2}} + r^{-\alpha} a_k \left\{ \frac{(1-\alpha)(1+3c\theta^2)s(\theta) - 2\beta(1+c\theta^2)(s_2\theta^2+2s_4\theta^4)}{1-(b^2-2\beta b^2-3c)\theta^2-(3-2\beta)b^2c\theta^4} \right\}$
Conditions for Restricted Linear Model:	$b^2 = \frac{\delta-3}{(\delta-1)(1-2\beta)}, \quad c = 0$
Conditions for Restricted Cubic Model:	$b^2 = \frac{3}{3-2\beta}, \quad c = \frac{2\beta\delta-3}{3-2\beta}$

of the experimental equation of state data of a quality comparable to that obtained with the MLSG equation (Levelt Sengers *et al.*, 1976). As an example we show in Fig. 10 a deviation plot when the chemical potential data for steam are fitted to the linear model; the corresponding deviation plot when fitted to the MLSG equation was given in Fig. 8. Unlike the MLSG equation, it is also possible to fit the linear model and the cubic model directly to the original pressure data (Murphy *et al.*, 1973, 1975).

A stringent test on the validity of any equation of state is the extent to which it is consistent with experimental specific heat data as well. However, efforts to describe experimental P-V-T data and C_V data simultaneously in terms of one scaled equation of state like the linear model, cubic model, or the MLSG equation have had only limited success (Lentini and Vicentini-Missoni, 1973; Huang and Ho, 1973; Barmatz *et al.*, 1975, White and Maccabee, 1975).

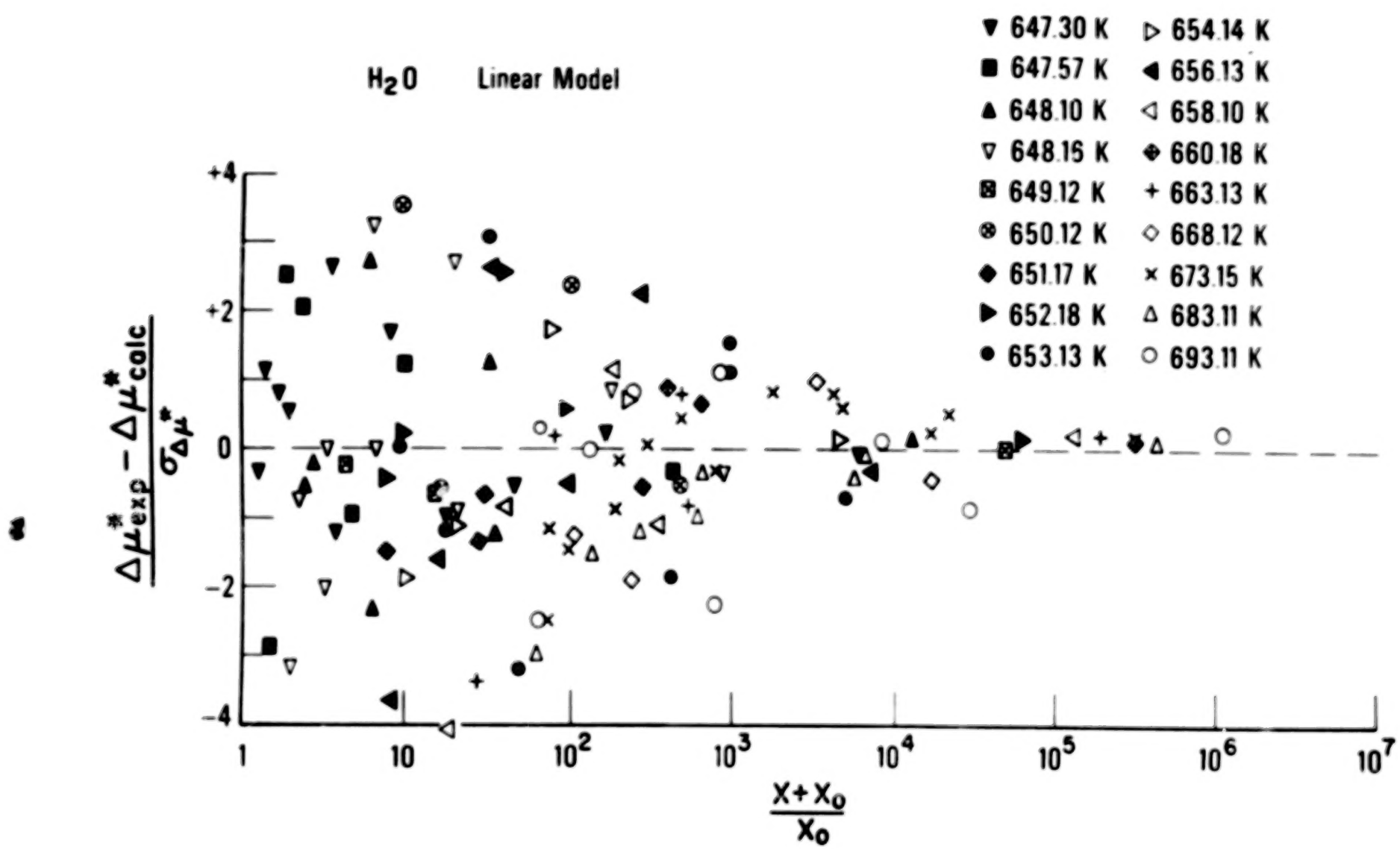

Figure 10. Plot of normalized deviations $(\Delta\mu^*_{exp} - \Delta\mu^*_{calc})/\sigma_{\Delta\mu^*}$ as a function of $(x+x_o)/x_o$ for H_2O (linear model). $\sigma_{\Delta\mu^*}$ is the estimated experimental uncertainty; $\Delta\mu^*_{calc}$ is calculated from the linear model with parameters ρ_c = 322.2 kg/m^3, T_c = 647.05 K, β = 0.350, δ = 4.50, k_1 = 1.664, b_1^2 = 1.4286, a_1 = 24.47 (Levelt Sengers *et al.*, 1976).

3.5 Universality of Critical Behavior

The theoretical studies of various model systems have led to the formulation of the hypothesis of universality. According to this hypothesis systems having the same basic symmetries are expected to have identical critical exponents and scaling functions, and are said to belong to the same universality class (Jasnow and Wortis, 1968; Watson, 1969, Griffiths, 1970; Kadanoff, 1971,1976; Betts *et al.*, 1971; Milošević and Stanley, 1972; Aharony, 1976). As discussed in Section 2.7 the hypothesis is supported by the renormalization group theory of critical phenomena.

Specifically, the universality hypothesis implies that systems belonging to the same universality class should asymptotically obey the same scaled equation of state apart from only two adjustable constants. That is, the critical exponents and the function $h(x/x_o)$ in (3.11) should be the same for all these systems leaving only two substance dependent parameters, namely D and x_o. Hence, the hypothesis predicts that scaling plots of $\Delta\mu^*/(\Delta\rho^*)|\Delta\rho^*|^{\delta-1}$ versus x/x_o for different fluids, such as the one shown in Fig. 7 for ^{4}He, can be made to coincide with proper choice of the adjustable scale factors D and x_o. In Fig. 11 we show that the scaling plots of five different gases, namely ^{3}He, ^{4}He, Xe, CO_2 and H_2O, can indeed be brought into one single universal curve, thus supporting the hypothesis of universality for these five gases (Levelt Sengers, 1974).

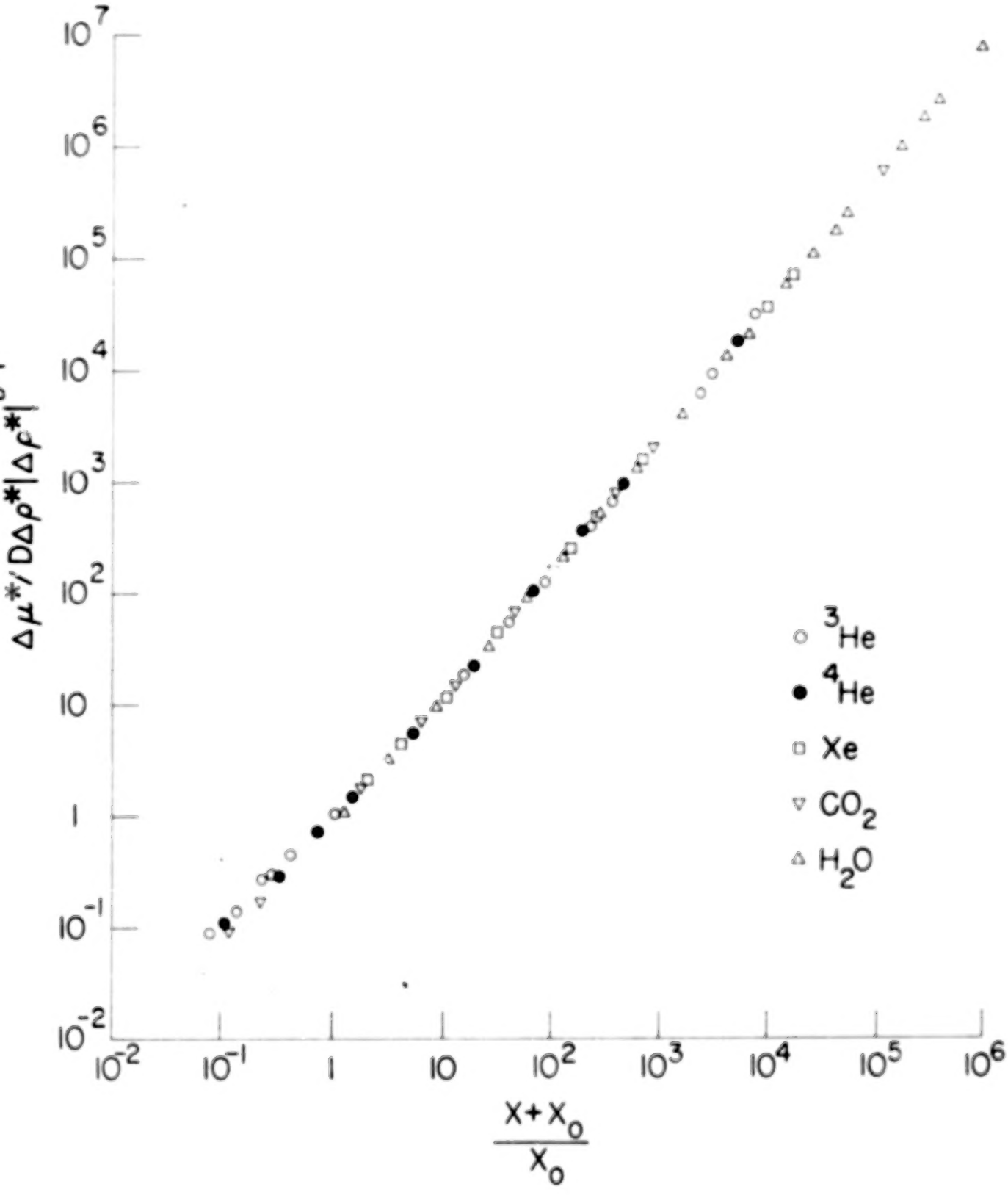

Figure 11. Scaled chemical potential data for ^{3}He, ^{4}He, Xe, CO_2 and H_2O as a function of $(x+x_0)/x_0$. Reduction parameters are taken from Table X.

In order to make a quantitative study of the validity of this hypothesis, it is necessary to use an explicit expression for the scaled equation of state. Using least-squares techniques, a goodness-of-fit criterion is then readily established in the form of the standard deviation; varying precision is taken care of by weighting, the deviations of the individual points are compared with their estimated standard error to check whether systematic errors are present and a number of parameters such as T_c, ρ_c, the critical exponents and the adjustable constants D and x_o are varied to optimize the fit (Levelt Sengers *et al.*, 1976).

The specific scaled equations of state described in the preceding section are only suitable candidates for a universal equation of state, if the number of adjustable parameters is restricted to two. Thus when in the MLSG (3.18) E_1 and x_o are treated as adjustable parameters, not only the critical exponents but also the constant E_2 must be independent of the fluid under consideration. In practice, E_2 turns out to be small and indeed roughly the same for a number of fluids.

Likewise, the principle of universality allows us to treat k_1 and a_1 in the linear model (3.21) as adjustable parameters, but the parameters b_1 must be kept at a fixed value. A popular choice for the parameter b_1 in the linear model is that recommended by Schofield, Litster and Ho [1969]

$$b_1^2 = \frac{\delta-3}{(\delta-1)(1-2\beta)} . \qquad (3.23)$$

With this choice for b_1^2 the representation of the singular part of the specific heat in terms of the linear model parameters reduces to

$$\frac{C_V^{\bullet}, \text{sing}}{T^{\bullet}} = \frac{A^+}{\alpha} r^{-\alpha} = a_1 k_1 \frac{(1-2\beta)\gamma(\gamma-1)(\delta-1)}{2\alpha(\delta-3)} r^{-\alpha} , \tag{3.24}$$

so that a contour of constant r may be interpreted as a contour of constant anomalous specific heat. We refer to the linear model with the special choice (3.23) for b_1^2 as the *restricted* linear model. If this special choice for b_1^2 is substituted in

$$E_2^{-1} = \left[\frac{b_1^{(\delta-3)/(\gamma-1)}}{b_1^2 - 1} \right]^{2\beta} - 1 , \tag{3.25}$$

one obtains a corresponding restricted version of the MLSG equation (Levelt Sengers *et al.*, 1976).

With the cubic model the compressibility χ_T can be made independent of θ by the choice (Ho and Litster, 1970)

$$b_2^2 = \frac{3}{3-2\beta}, \quad c = \frac{2\beta\delta-3}{3-2\beta} . \tag{3.26}$$

For this *restricted* cubic model

$$\chi_T^{\bullet} = \frac{k_2}{a_2} r^{-\gamma}, \tag{3.27}$$

and contours of constant r correspond to contours of constant compressibility $\chi_T^{\bullet}$.

It has been found that the cubic model does yield a satisfactory representation of the equation of state data for the 3-dimensional

Ising model though with values of b_2^2 and c that differ from the choice (3.26) (Wallace and Zia, 1974; Tarko and Fisher, 1975; Wallace, 1976).

To investigate the hypothesis of universality for fluids we made a statistical analysis of the equation of state data for ^{3}He (Wallace and Meyer, 1970), ^{4}He (Roach, 1968), Xe (Habgood and Schneider, 1954), CO_2 (Michels *et al.*, 1937), H_2O (Rivkin *et al.*, 1962, 1963, 1964, 1966) and density profile data for O_2 (Weber, 1970). It was found that the experimental data of all these fluids could be fitted to the same scaled equation of state for which we chose the restricted linear model. With the exception of O_2 the range of the fits corresponded approximately to

$$5 \times 10^{-4} \leq |\Delta T^*| \leq 3 \times 10^{-2} \ , \ |\Delta \rho^*| \leq 0.25 \ . \tag{3.28}$$

In this range the critical exponents of those fluids were compatible with the "universal" values (Levelt Sengers and Sengers, 1975)

$$\begin{aligned} \alpha &= 0.10 \pm 0.04 \quad & \beta &= 0.355 \pm 0.007 \ , \\ \gamma &= 1.19 \pm 0.03 \quad & \delta &= 4.35 \pm 0.10 \ . \end{aligned} \tag{3.29}$$

These exponent values are similar to the values found by other authors for ^{3}He (Wallace and Meyer, 1970); Chase and Zimmerman, 1973), ^{4}He (Roach, 1968; Moldover, 1969; Brown and Meyer, 1972; Kierstead, 1973; Tomasaga, 1974), Ar (Lin and Schmidt, 1974a; Wu and Pings, 1976), Kr (Gulari and Pings, 1973), Xe (Edwards *et al.*, 1968; Smith *et al.*, 1971; Cornfeld and Carr, 1972; Thoen and Garland, 1974), CO_2 (Lipa *et al.*, 1970; Levelt Sengers *et al.*, 1971; Murphy *et al.*, 1973; White and

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Maccabee, 1975), N_2O and $CClF_3$ (Levelt Sengers *et al.*, 1971) and reviewed elsewhere (Levelt Sengers, 1974).

If we represent the equation of state data in the range (3.28) by a scaled equation of state with the exponent values (3.29) and *assume* universality between fluids, we may then try to impose the same equation of state with the same exponents upon the data for other fluids and determine the resulting values for the two remaining adjustable parameters. Equation of state parameters thus obtained for a variety of fluids in terms of a universal equation of state (restricted MLSG equation, restricted linear model and restricted cubic model) are presented in Table X. The parameters should be treated as informed estimates corresponding to the range (3.28). For accurate calculations one should return to the parameter values obtained in the original statistical fits to the data of the individual fluids (Levelt Sengers *et al.*, 1976). The last column of Table X contains correlation length parameters to be discussed in Section 5.7.

The hypothesis of universality implies also universality for the amplitude ratios Γ/Γ', $\Gamma_{DB}^{\delta-1}$ and A^+/A_{II}^- (cf. Table VIII). The parameter values given in Table X yield $\Gamma/\Gamma' = 4.0$, $\Gamma_{DB}^{\delta-1} = 1.5$ and $A^+/A_{II}^- = 0.47$ to be compared with the values $\Gamma/\Gamma' = 5.07$, $\Gamma_{DB}^{\delta-1} = 1.7$ and $A^+/A_{II}^- = 0.51$ for the 3-dimensional Ising model (Aharony and Hohenberg, 1976).

Table X

Critical Region Parameters for a Number of Fluids Assuming Effective Universal Exponents

	Critical Point Parameters			MLSG Equation		Restricted Linear Model		Cubic Model		Correlation Length Parameters
	P_c MPa	ρ_c kg/m^3	T_c K	x_0	E_1	k_1	a_1	k_2	a_2	ξ_0 Å
^{3}He	0.11678	41.45	3.3099	0.489	2.96	0.924	4.58	0.818	4.05	2.7
^{4}He	0.22742	69.6	5.1895	0.369	2.67	1.021	6.40	0.904	5.66	2.2
Ar	4.865	535	150.725	0.183	2.27	1.309	16.1	1.160	14.2	1.6
Kr	5.4931	908	209.286	0.183	2.27	1.309	16.1	1.160	14.2	1.7
Xe	5.8400	1110	289.734	0.183	2.27	1.309	16.1	1.160	14.2	1.9
p-H_2	1.285	31.39	32.935	0.260	2.34	1.156	9.6	1.024	8.5	1.9
N_2	3.398	313.9	126.24	0.164	2.17	1.361	18.2	1.206	16.1	1.6
O_2	5.043	436.2	154.580	0.183	2.21	1.309	15.6	1.160	13.9	1.6
H_2O	22.06	322.2	647.13	0.100	1.20	1.622	21.6	1.438	19.1	1.3
D_2O	21.66	357	643.89	0.100	1.20	1.622	21.6	1.438	19.1	1.3
CO_2	7.3753	467.8	304.127	0.141	2.01	1.436	21.3	1.273	18.9	1.6
NH_3	11.303	235	405.4	0.109	1.37	1.573	21.4	1.394	19.1	1.4
SF_6	3.7605	730	318.687	0.172	3.08	1.337	23.9	1.185	21.2	2.0
CH_4	4.595	162.7	190.555	0.164	2.03	1.361	17.0	1.206	15.1	1.7
C_2H_4	5.0390	215	282.344	0.168	2.17	1.350	17.5	1.197	15.5	1.9
C_2H_6	4.8718	206.5	305.33	0.147	2.03	1.416	20.2	1.255	17.9	1.8
C_3H_8	4.247	221	369.82	0.137	1.83	1.451	20.2	1.286	17.9	2.0

Notes: $\alpha = 0.100$ $\beta = 0.355$ $b_2^2 = 1.3100$ $\nu = 0.633$

$\gamma = 1.190$ $\delta = 4.352$ $E_2 = 0.287$ $b_1^2 = 1.3909$ $c = 0.0393$ $2-\eta = 1.879$

3.6 Questions Raised by Experiments

According to the hypothesis of universality fluids are expected to belong to the same universality class as the Ising model and the Landau-Ginsburg-Wilson model. In the previous section we arrived at the conclusion that the experimental PVT data of six fluids could be represented in the temperature range $5 \times 10^{-4} \leq |\Delta T^*| \leq 3 \times 10^{-2}$ by a universal scaled equation of state with exponent values $\beta = 0.355 \pm 0.007$ and $\gamma = 1.19 \pm 0.03$. However, these exponent values exclude the values quoted in (2.64) and (2.78) for this universality class.

The picture of universality of fluid critical behavior with the exponent values found in (3.29) has to be challenged as soon as, for at least one fluid, a different critical exponent value is found. Such experimental challenges do exist. One example is the exponent for the coexistence curve of SF_6 which has been measured in three independent experiments (Balzarini and Ohrn, 1972; Rathjen and Straub, 1973; Weiner *et al.*, 1974). In each case, a value of β near 0.34 was found; in the last case, the value of β was 0.340 ± 0.001 in the range $2 \times 10^{-5} < |\Delta T^*| < 5 \times 10^{-2}$. In binary liquids, to be discussed in Section 4.5, a value of β near 0.34 is the rule rather than the exception (Stein and Allen, 1974).

With respect to the exponent γ, the value $\gamma = 1.19 \pm 0.03$ in (3.28) is to be compared with a value $\gamma = 1.14$ recently deduced for ^3He by Behringer, Dorion and Meyer [1976] from highly accurate PVT data, with a value $\gamma = 1.19 \pm 0.01$ determined for C_2H_4 by Hastings and Levelt Sengers [1976] from precise PVT data, and with γ values of about $\gamma = 1.22$ from light scattering data that are usually obtained at temperatures closer to T_c (Puglielli and Ford, 1970; Knacek and Cannell, 1971; Cannell, 1975).

The most serious challenge, however, has come from the study of gravity-induced density gradients by optical techniques developed by Wilcox and coworkers and discussed in Section 2.7. From an optical study of the coexistence curve of SF_6 Balzarini and Ohrn [1972] noted that the exponent β decreases when the temperature range is reduced. Very recently, Hocken and Moldover [1976] measured density gradient profiles in Xe, CO_2 and SF_6 in the range $-1.5 \times 10^{-5} < |\Delta T^*| < 5 \times 10^{-5}$. Analyzing the data in terms of a scaled equation of state, they obtained β values around 0.324 and γ values around 1.25, indicating that the critical exponents of fluids do approach Ising-like values sufficiently close to the critical point. Since these exponent values are only attained for $|\Delta T^*| < 10^{-4}$, it must be concluded that corrections to asymptotic scaling must be present in the entire range where conventional PVT experiments are accurate. Since these correction terms may vary from fluid to fluid, they may cause the deviations from universality of the apparent critical exponents determined in the conventional ranges.

3.7 Scaling Fields and Corrections to Scaling

The treatment of the thermodynamic behavior of fluids in the critical region outlined in the preceding sections has been challenged by theory in two respects. The first challenge pertains to the choice of scaling variables and the second one regards the corrections to be applied when the range of the asymptotic validity of the scaling laws is exceeded.

The choice of variables is best discussed in terms of intensive or "field" variables, P, μ and T. It can be readily verified that the thermodynamic scaling laws formulated in Section 3.3 are equivalent to the statement in terms of field variables that the pressure has the form

$$P^* = P^*_{sing}(\Delta\mu^*,\Delta T^*) + \Delta\mu^* - A^*_o(T^*) \ , \tag{3.30}$$

with

$$P^*_{sing}(\Delta\mu^*,\Delta T^*) = |\Delta T^*|^{2-\alpha} f(\Delta\mu^*/|\Delta T^*|^{\beta\delta}) \ . \tag{3.31}$$

In the plane of the independent field variables μ^* and T^* one direction is singled out as special, namely the slope $c_1 = d\mu^*_{cxc}/dT^*$ of the coexistence curve at the critical point. To linear order in ΔT^* our first scaling field $\Delta\mu^*$ has the form $\Delta\mu^* = \mu^* - \mu_c^* - c_1\Delta T^*$, where $\mu_c^* = \mu^*(\rho_c,T_c)$. As the second scaling field in (3.31) we simply chose the temperature difference ΔT^*. There is, however, no physical reason why this second scaling field could also not be a function of $\mu^*-\mu_c^*$ and ΔT^*. In fact, the renormalization group theory of critical phenomena indicates that the singular part of the pressure, which is

analogous to the free energy of a spin system discussed in Section 2.7, will in general have the form (Wegner, 1972; Rehr and Mermin, 1973);

$$P^*_{sing}(u_h,u_t) = |u_t|^{2-\alpha} f(u_h/|u_t|^{\beta\delta}) \ , \tag{3.32}$$

where the scaling fields u_h and u_t are analytic functions of μ^* and T^*

$$\begin{aligned} u_h &= (\mu^*-\mu_c^*) - c_1\Delta T^* + \ldots \ , \\ u_t &= \Delta T^* - c_2(\mu^*-\mu_c^*) + \ldots \ . \end{aligned} \tag{3.33}$$

The term $\Delta\mu^* - A_o^*(T^*)$ in (3.30) represents an analytic background term in terms of the field variables ΔT^* and $\Delta\mu^*$. Allowing for a more general analytic background one obtains a revised scaled equation of the form

$$P^* = |u_t|^{2-\alpha} f(u_h/|u_t|^{\beta\delta}) + \sum_{ij}\sum P_{ij}(\Delta T^*)^i(\mu^*-\mu_c^*)^j, \tag{3.34}$$

with $P_{00} = P_c^* = 1$ and $P_{01} = \rho_c^* = 1$.

This equation reduces asymptotically to (3.30). However, the revised equation (3.34) with the scaling fields (3.33) leads to some additional features not contained in (3.30). In particular, the expression for the coexistence densities implied by (3.34) has, in addition to the leading term of the form $|\Delta T^*|^{\beta}$, a correction term with the entropy-like structure $|\Delta T^*|^{1-\alpha}$ (Widom and Rowlinson, 1970; Rehr and Mermin, 1973). This term drops out when the difference $\rho^*_{liq} - \rho^*_{vap}$ is formed, but it persists in the sum $\rho^*_{liq} + \rho^*_{vap}$. Hence, it is

predicted that the coexistence curve diameter is not straight, but that it has a small "hook" at the critical point. Thus far this hook has been observed in one experiment only (Weiner *et al.*, 1974), but the theoretical arguments in favor of its existence in all fluids are rather strong. The reason that it has almost always escaped experimental detection is probably due to the fact that the $|\Delta T^*|^{1-\alpha}$ term is followed by a (ΔT^*) term, so that the effect of the former is only visible extremely close to the critical point (Zollweg and Mulholland, 1972). The hook on the diameter implies that critical densities estimated by extrapolating the rectilinear diameter are overestimated, but the error is generally less than 0.5%. The effects of the different choices of scaling fields in the behavior of fluids in the one-phase region have not yet been studied in any detail.

We now turn to the so-called corrections to scaling. Suppose that the scaling fields u_h and u_t have been defined properly and that the scaling hypothesis (3.32) is made. Then one can expect this hypothesis to be valid only in a limited range around the critical point. The renormalization group approach to the theory of critical phenomena also provides estimates of the form and the size of the correction terms beyond the asymptotic range, as pointed out by Wegner [1972]. They are obtained by retaining in (2.75) not only the relevant scaling fields $u_1 = u_h$ and $u_2 = u_t$, but also irrelevant scaling fields u_3, u_4 . . . . In analogy to the free energy of a spin system the singular part of the pressure then assumes the form (Wegner, 1972; Ley-Koo and Green, 1976)

$$P^*_{sing}(u_h, u_t, u_3, u_4, \ldots) = |u_t|^{2-\alpha} f(u_h|u_t|^{-\beta\delta}, u_3|u_t|^{\Delta_1}, u_4|u_t^{\Delta_2}, \ldots) \, . \tag{3.35}$$

Unlike the relevant scaling field u_h and u_t, the irrelevant scaling fields do not approach zero at the critical point. They scale with different powers of u_t, indicated by the so-called gap exponents Δ_1, Δ_2, ... These gap exponents are again expected to be universal. Current estimates of the first two gap exponents for Ising-like systems in three dimensions are $\Delta_1 = 0.50$ and $\Delta_2 = 1.5$ (Golner and Riedel, 1975, Saul *et al.*, 1975, Baker *et al.*, 1976, Camp *et al.*, 1976).

The irrelevant scaling fields do not contribute to the leading anomalies at the critical point, but they do lead to corrections to the asymptotic scaling laws. For instance, the expansions for the coexisting densities obtain the form (Ley-Koo and Green, 1976):

$$\frac{\Delta\rho^*_{liq} + \Delta\rho^*_{vap}}{2} = B_{M1}|\Delta T^*|^{1-\alpha} + P_{11}\Delta T^* + B_{C3}|\Delta T^*|^{1-\alpha+\Delta_1} + \ldots \, , \tag{3.36}$$

$$\frac{\Delta\rho^*_{liq} - \Delta\rho^*_{vap}}{2} = B|\Delta T^*|^{\beta} + B_{C1}|\Delta T^*|^{\beta+\Delta_1} + B_{C2}|\Delta T^*|^{\beta+2\Delta_1} + B_{M2}|\Delta T^*|^{\beta+1} + \ldots \, . \tag{3.37}$$

where the coefficients with subscript M refer to terms originating from "mixing" the μ and T variables in forming the scaling fields and those with subscript C to corrections to scaling.

3.8 Assessment of Status of Fluid Critical Behavior

As discussed in Sections 3.4 and 3.5, when equation of state data of fluids are considered in a range of ±0.25 in $\Delta\rho^*$ and ±0.03 in ΔT^*, the data can usually be represented in terms of a simple scaled equation of state with critical exponents that vary only slightly from fluid to fluid, but that are distinctly different from those of the Ising model. However, recent optical experiments at $|\Delta T^*| < 5 \times 10^{-5}$ have shown that in that range the fluid critical exponents are approaching those for the Ising model (Hocken and Moldover, 1976).

The optical data can be reconciled with the data obtained in more conventional ranges if a Wegner expansion (3.35) with a sufficient number of terms is used. Since the gap exponent in this expansion is small and the coefficients are expected to be of order unity, the Wegner expansion will converge only slowly and a large number of terms will contribute in the range $10^{-4} < |\Delta T^*| < 10^{-1}$. Ley-Koo and Green (1976) recently fitted the difference of coexisting densities of SF_6. They found that a simple power law $B|\Delta T^*|^{\beta}$ with $\beta = 0.327 \pm 0.003$ was restricted to a range $|\Delta T^*| < 7 \times 10^{-4}$. A temperature range $|\Delta T^*| < 2 \times 10^{-2}$ already required three terms in the expansions (3.36) and (3.37). Had they imposed the value $\beta = 0.312$ suggested from series expansions for Ising-like systems, the asymptotic range would have been even smaller and more correction terms would have been required. A value for β slightly larger than 0.312 is thus supported by the optical experiments of Hocken and Moldover [1976], by an

analysis of the coexistence curve data for SF_6 (Ley-Koo and Green, 1976) and, as we shall see in Section 4.5, by data on coexisting phases in partially miscible binaries.

A value of β slightly larger than 0.312 is also supported by calculations on the basis of the renormalization group theory. As quoted in (2.78) the calculations of Baker *et al*. (1976) yield $\beta = 0.320 \pm 0.015$. Exponent values recently calculated by Golner and Riedel imply $\beta = 0.322$ with undetermined error. It is as yet not clear how the small discrepancy with the series expansion estimate for the exponent β will be resolved.

From a practical point of view, the representation of the thermodynamic data of fluids by a Wegner expansion in extended ranges around the critical point will be quite involved and unappealing. Hence, it is expected that the phenomenological expressions with effective exponents present in Section 3.5 will remain useful for many practical purposes.

IV. Critical Phenomena in Fluid Mixtures

4.1 Phase Transitions in Fluid Mixtures

In the one-phase region, a fluid mixture of n components possesses n+1 thermodynamic degrees of freedom. For two phases to coexist, the number of degrees of freedom is reduced by one. The intensive or field variables are the same in the two coexisting phases. The thermodynamic states with two coexisting phases correspond to a n-dimensional surface in the (n+1)-dimensional space of independent field variables. The condition of criticality is that the two coexisting phases become identical; this condition reduces again the number of available degrees of freedom by one. Thus the n-dimensional coexistence surface may terminate in a (n-1)-dimensional critical surface.

As an example we show schematically in Fig. 12 the geometry of the gas-liquid transition in a binary fluid in the 3-dimensional space of independent field variables. Since the chemical potentials μ_1 and μ_2 of the two components diverge to $-\infty$ at infinite dilution, it is often convenient to use instead the fugacities $f_1 = \exp(\mu_1/k_B T)$ and $f_2 = \exp(\mu_2/k_B T)$. As the three independent field variables we choose P, T and f_2. The coexistence surface is a 2-dimensional surface that terminates in a 1-dimensional critical line. The vapor-liquid critical points located on the critical line are called "plait points", a term dating back to Van der Waals. In this particularly simple example the critical line connects the critical points of the two pure fluids. In many cases, the critical line is interrupted and more complicated phase behavior results. The interested reader is referred to some excellent reviews on this subject (Kay, 1968; Rowlinson, 1969; Schneider, 1970,1972; Scott, 1972; Streett, 1974; Hicks and Young, 1975).

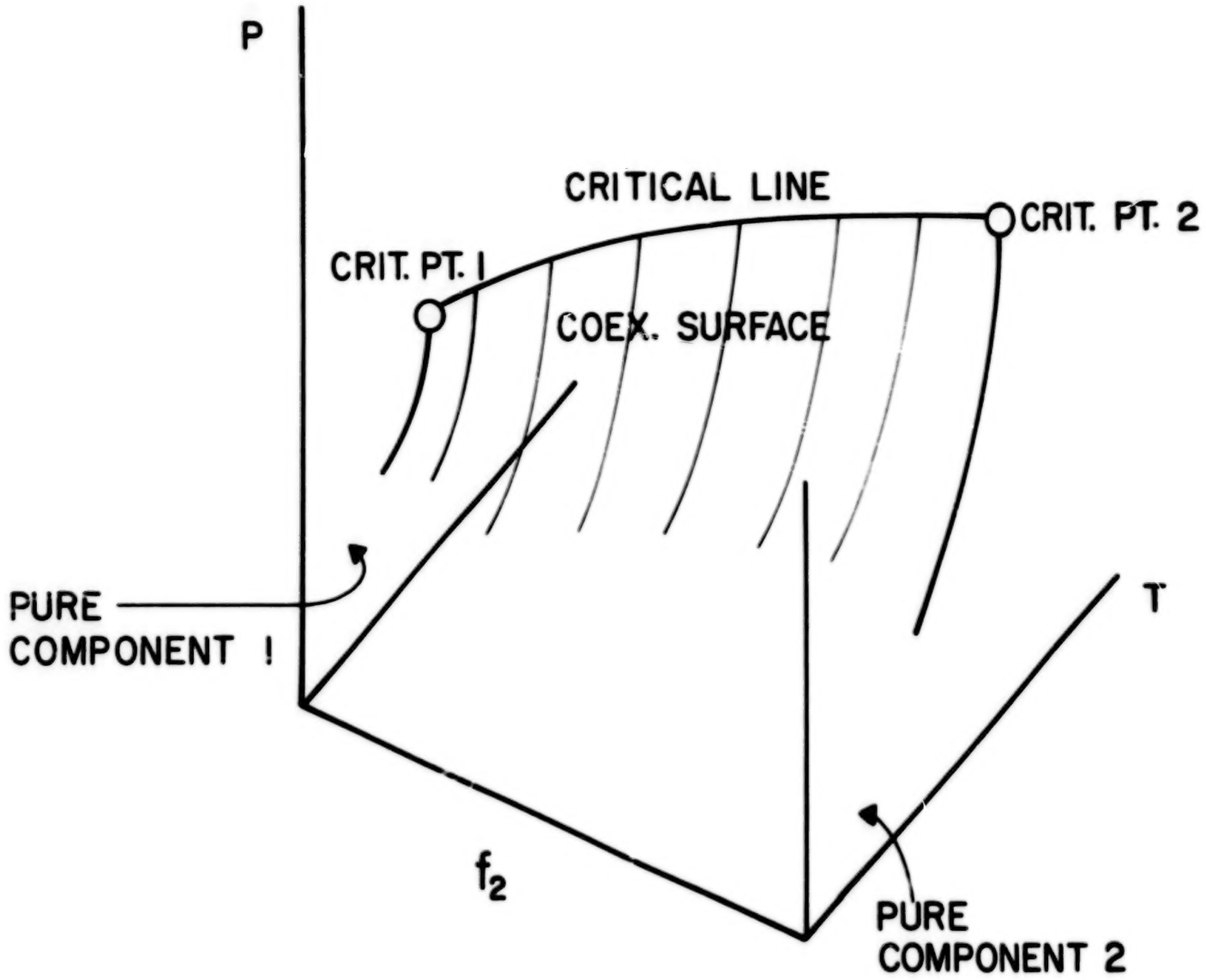

Figure 12. The gas-liquid coexistence surface and critical line of a binary fluid in the space of independent field variables pressure P, temperature T and fugacity f_2.

In addition to the coexistence of a vapor and a liquid in a binary fluid, there exists also the possibility that two liquid phases of different composition coexist. This gives rise to another coexistence surface in the space of independent field variables. Such binary liquids are usually studied in the presence of a vapor phase; the resulting system has one degree of freedom and traces a curve on the coexistence surface. The possibility exists for the two liquid phases to become identical; such a critical point is called a consolute point. This point is part of a line of consolute points terminating the coexistence surface. In P-T space, the line of consolute points is usually very steep, since the pressure has only a small effect on the critical solution temperature. In general, the plait point critical curve and the consolute critical curve are separated, but examples exist where one curve goes continuously over into the other. In some cases where the critical points of the two pure components are not connected, the critical line, starting from the critical point of the least volatile component (i.e. the one with the higher T_c and P_c) moves up to higher temperatures and pressures. Since a phase separation now occurs at temperatures and pressures above the critical ones of both components, one speaks about gas-gas equilibria. The simplest systems in which gas-gas separation occurs are mixtures of light and heavy noble gases. They have been the subject of several recent studies (De Swaan Arons and Diepen, 1966; Streett, 1965, 1967; Trappeniers and Schouten, 1974).

Although the variety of phase behavior, even for systems of two components, may seem somewhat bewildering, the description of critical-region phase behavior in multicomponent fluids is basically simple.

Particular insight is provided by the theory of Griffiths and Wheeler [1970] who developed the geometry of the critical region in the space of field variables. If we exclude a special direction of any coordinate axis, the critical behavior of a binary fluid at any type of critical point is a straightforward generalization of that in a one-component fluid, while no new features are introduced when three- or more-component fluids are considered.

Special orientations occur when critical lines pass through maxima or minima in temperature or pressure, or when critical azeotropy is encountered. Azeotropy occurs in binary fluids when two coexisting phases, which in general have different values of all extensive variables or densities, happen to have the same concentration. An azeotrope may trace out a curve on the coexistence surface; if it reaches the critical line one speaks of critical azeotropy. All these cases are considered separately in the theory of Griffiths and Wheeler. A brief account of this theory is given in the subsequent sections.

4.2 Introduction to Theory of Griffiths and Wheeler

Griffiths and Wheeler [1970] developed a description of thermodynamic behavior in the vicinity of critical surfaces in multicomponent systems that leads to a classification of the types of divergences to be expected in certain thermodynamic derivatives. The theory is most easily introduced by first reconsidering the description of the thermodynamic behavior near the critical point of a one-component fluid in terms of field variables. As the independent field variables we take

temperature and pressure and as dependent field variable the chemical potential.† We have seen that the slope of the vapor pressure curve (coexistence curve in the P-T plane) has a finite limiting value at the critical point and the P- and T-axis do not have a special direction parallel to this coexistence curve. In addition we note that the second derivatives $-(\partial^2\mu/\partial T^2)_p = \tilde{C}_p/T$ and $-(\partial^2\mu/\partial P^2)_T = \tilde{V}K_T$ diverge strongly at the critical point as discussed in Section I. *It is concluded that second derivatives of the dependent field variable with respect to directions that are oblique to the coexistence surface are strongly divergent.*

Next we consider a second derivative of μ taken along the coexistence surface, i.e. coexistence curve for a one-component fluid. For this purpose Griffiths and Wheeler introduce the thermodynamic identity

$$-\left(\frac{\partial^2\mu}{\partial T^2}\right)_Y = \frac{\tilde{C}_V}{T} + \tilde{V}K_T\left[\left(\frac{\partial P}{\partial T}\right)_Y - \left(\frac{\partial P}{\partial T}\right)_V\right]^2 , \qquad (4.1)$$

where Y is any direction in the P-T plane. It is seen that $\partial^2\mu/\partial T^2$ will diverge strongly, as K_T, for any direction Y that does not coincide with the direction of the critical isochore $V = V_c$. However, if the direction Y does coincide with that of the critical isochore at the critical point, then the term in brackets vanishes and $\partial^2\mu/\partial T^2$ will

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†In Sections II, III and V the chemical potential is taken per particle. In this section we find it more convenient to take the chemical potential per mole. Molar values of extensive thermodynamic quantities are indicated by a tilde.

diverge only weakly, as C_V. Thus, a second derivative taken in this special direction is a derivative in which an extensive variable or "density" (V) rather than a field (P) is kept constant.

It remains to be shown that the direction $V = V_c$ is asymptotically the same as that of the coexistence curve. We have seen that this is indeed the case for the classical equations and the lattice gas. In general, one makes use of the thermodynamic identity

$$\left(\frac{dV}{dT}\right)_{cxc} = \left[\left(\frac{dP}{dT}\right)_{cxc} - \left(\frac{\partial P}{\partial T}\right)_V\right]\left(\frac{\partial V}{\partial P}\right)_T , \qquad (4.2)$$

which relates the slope dV/dT and the compressibility $(\partial V/\partial P)_T$ on either side of the phase boundary. The slope dV/dT has a different sign on the two sides of the phase boundary, but the compressibility has the same sign. Thus the term in square brackets must vanish at the critical point and, in fact, it must go to zero as $|\Delta T^*|^{\gamma+\beta-1}$. Thus the continuity of the slope of the vapor pressure curve and the critical isochore at the critical point holds for real fluids as well. *It is concluded that second derivatives of the dependent field variable with respect to the independent ones, but taken along the coexistence surface, are in fact derivatives in which a density is held constant and that these derivatives diverge weakly.*

Finally in multicomponent fluids a third direction exists, namely the one along the critical surface. One-component fluids do not provide us with any clues for the behavior of derivatives along this additional direction. However, we have seen that in binary fluids critical lines are smooth curves in field space. We thus expect second derivatives

taken in this direction to be nondivergent; as we shall see, they correspond to derivatives in which not one but two densities are held constant.

4.3 Classification of Thermodynamic Anomalies in Fluid Mixtures

In order to make the ideas about the geometry of critical-point phase transitions in mixtures more precise, Griffiths and Wheeler considered the properties of the compliance matrix introduced in Section I. We have seen that second derivatives with respect to the field variables,

$$D(P) = -(\partial^2\mu/\partial P^2)_T \ , \ D(T) = -(\partial^2\mu/\partial T^2)_P \ , \tag{4.3}$$

are strongly divergent if no special geometric relation exists between the field variables and the coexistence surface or the critical surface. Although each element of the compliance matrix diverges strongly, its determinant $D(T,P) = VK_TC_V/T$ is seen to diverge only as the product of a strongly (K_T) and a weakly (C_V) diverging quantity. The factor K_T corresponds to a second derivative taken at an angle with the coexistence curve. For an n-component mixture, the determinant of the full (n+1) by (n+1) compliance matrix is still no more divergent than strongly times weakly because, in the space of independent field variables, a base can be chosen with only one vector at an angle to the coexistence surface ("strong" direction) and only one vector in the coexistence surface, but not in the critical surface ("weak" direction). Thus the behavior near a critical point in a multicomponent mixture is no more complicated than critical behavior in a binary mixture.

Similar considerations can be applied to any subset A of m independent field variables with $m \leq n+1$. If in this subset a base can be chosen such that one vector is oblique to the coexistence surface and one lies in the critical surface, then the determinant D(A) of the matrix of corresponding second derivatives will be strongly times weakly divergent. If the base lacks a vector oblique to the coexistence surface, D(A) is weakly divergent. If it contains a vector oblique to the coexistence surface but lacks one in the critical surface, then D(A) is strongly divergent. If the base has no vectors other than in the critical surface, D(A) is nondivergent.

As an example, let us consider a binary mixture with field variables T, P, μ_1, μ_2. As the dependent variable we consider $-\mu_2(T,-P,\Delta)$ as a function of T, -P and $\Delta = \mu_1 - \mu_2$. In terms of these variables the Gibbs-Duhem equation assumes the form

$$d(-\mu_2) = \tilde{S}dT + \tilde{V}d(-P) + Xd\Delta \ , \tag{4.4}$$

where X is the mole fraction of component 1. The second derivatives

$$\tilde{C}_{P\Delta}/T = -\left(\frac{\partial^2\mu_2}{\partial T^2}\right)_{P\Delta}, \ \tilde{V}K_{T\Delta} = -\left(\frac{\partial^2\mu_2}{\partial P^2}\right)_{T\Delta}, \ \chi_{TP} = -\left(\frac{\partial^2\mu_2}{\partial\Delta^2}\right)_{TP} \ , \tag{4.5}$$

are expected to diverge strongly, since the derivatives are taken in directions that are oblique to the coexistence surface. In the terminology developed above, these quantities are of the form D(A) where A is a single vector not parallel to the coexistence surface.

However, with the exception of χ_{TP} which can be studied by light scattering, derivatives with two fields constant are usually not very accessible to the experimenter who tends to conduct measurements at

constant concentration rather than at constant Δ. Hence, one is more interested in the behavior of derivatives like K_{TX}, K_{SX}, C_{PX}, and C_{VX}, i.e. derivatives in which one or more densities are held constant. Using Jacobians such derivatives can be expressed in terms of ratios of determinants of matrices of second derivatives, as pointed out by Griffiths and Wheeler [197C]. A few examples will suffice to give the general idea:

$$\tilde{V}K_{TX} = -\left(\frac{\partial \tilde{V}}{\partial P}\right)_{TX} = -\frac{\partial(\tilde{V}X)}{\partial(P\Delta)} \cdot \frac{\partial(P\Delta)}{\partial(PX)} = -\frac{\partial(\tilde{V}X)}{\partial(P\Delta)} \Big/ \frac{\partial X}{\partial \Delta} = \frac{D(P\Delta)}{D(\Delta)}, \qquad (4.6a)$$

and, likewise,

$$\frac{\tilde{C}_{PX}}{T} = \frac{D(T\Delta)}{D(\Delta)} . \qquad (4.6b)$$

A second derivative with one density constant, such as K_{TX} or C_{PX}, can be written as the quotient of a determinant, such as $D(P\Delta)$ or $D(T\Delta)$ which diverges strongly times weakly, and a determinant, such as $D(\Delta)$ which is strongly divergent. Hence we expect derivatives with one density held constant to be weakly divergent. A derivative at constant density is taken along a path asymptotically parallel to the coexistence surface.

Derivatives in which two densities are held constant can be handled in a similar manner. For example

$$\tilde{V}K_{SX} = -\left(\frac{\partial \tilde{V}}{\partial P}\right)_{SX} = -\frac{\partial(\tilde{V}\tilde{S}X)}{\partial(TP\Delta)} \cdot \frac{\partial(T\Delta)}{\partial(\tilde{S}X)} = \frac{D(TP\Delta)}{D(T\Delta)} , \qquad (4.7a)$$

and, likewise,

$$\frac{\tilde{C}_{VX}}{T} = \frac{D(TP\Delta)}{D(P\Delta)} \quad . \tag{4.7b}$$

Since both determinants diverge strongly times weakly, we expect the derivatives with two densities held constant to be nondivergent. These derivatives are taken along a path that lies asymptotically in the critical surface.

We should expect exceptions to these rules when the critical surface or the coexistence surface bears a special relation to any of the coordinate axes. For instance, critical lines often pass through pressure extrema as a function of Δ. At such an extremum the critical curve is parallel to the T-Δ plane. In this plane we can choose a base with one vector parallel to the critical line and one vector at an angle to the coexistence surface. As a consequence $D(T\Delta)$ no longer diverges strongly times weakly, but is only strongly divergent. Thus we conclude from (4.6b) and (4.7a) that C_{PX} is nondivergent and VK_{SX} weakly divergent, just the opposite of the general case. Similarly if a critical line goes through an extremum in temperature, $D(P\Delta)$ is strongly divergent and we conclude that VK_{TX} is nondivergent, while C_{VX} is weakly divergent, again the reverse of the general case.

Along an azeotrope the volumes of the two coexisting phases, $\tilde{v} = (\partial\mu_2/\partial P)_{T\Delta}$, and the entropies, $\tilde{s} = -(\partial\mu_2/\partial T)_{P\Delta}$ are unequal, while the concentrations $X = -(\partial\mu_2/\partial\Delta)_{PT}$ are the same. By applying (4.4) to the two coexisting phases it can be readily shown that under these conditions

$$\left(\frac{\partial P}{\partial \Delta}\right)_T = \left(\frac{\partial T}{\partial \Delta}\right)_P = 0 \ . \tag{4.8}$$

Thus the coexistence surface is parallel to the Δ-axis and $D(\Delta)$ is weakly divergent in the case of critical azeotropy. From (4.6) we conclude that K_{TX} and C_{PX} are strongly divergent as in a one-component fluid, while C_{VX} remains finite. Other cases of exceptional orientation of a coordinate axis with respect to the coexistence surface can be treated in a similar manner.

The thermodynamics of binary mixtures near the gas-liquid critical line was also considered by Saam [1970].

4.4 Thermodynamic Behavior Near a Critical Line in Binary Fluids in Terms of Scaling Laws

A procedure for describing the critical behavior of binary fluids using scaling laws was recently developed by Leung and Griffiths [1973]. They consider the case where the critical line connects the critical points of the two pure fluids as indicated in Fig. 12 and Fig. 13. As the dependent field variable they take the pressure P; as the independent field variables they take the temperature T and two variables Θ and ζ which are related to the fugacities f_1 and f_2 by

$$\Theta = c_1 f_1 + c_2 f_2 \ , \ \zeta = c_2 f_2 / \Theta \ , \tag{4.9}$$

where c_1 and c_2 are positive constants. The value $\zeta = 0$ corresponds to the pure fluid 1 and the value $\zeta = 1$ corresponds to the pure fluid 2. The critical line may be characterized by $T_c(\zeta)$. We now consider the behavior of the mixture as a function of T and Θ for a given value of ζ (see Fig. 13). The intersection of the coexistence surface with a plane ζ = constant defines a coexistence curve that

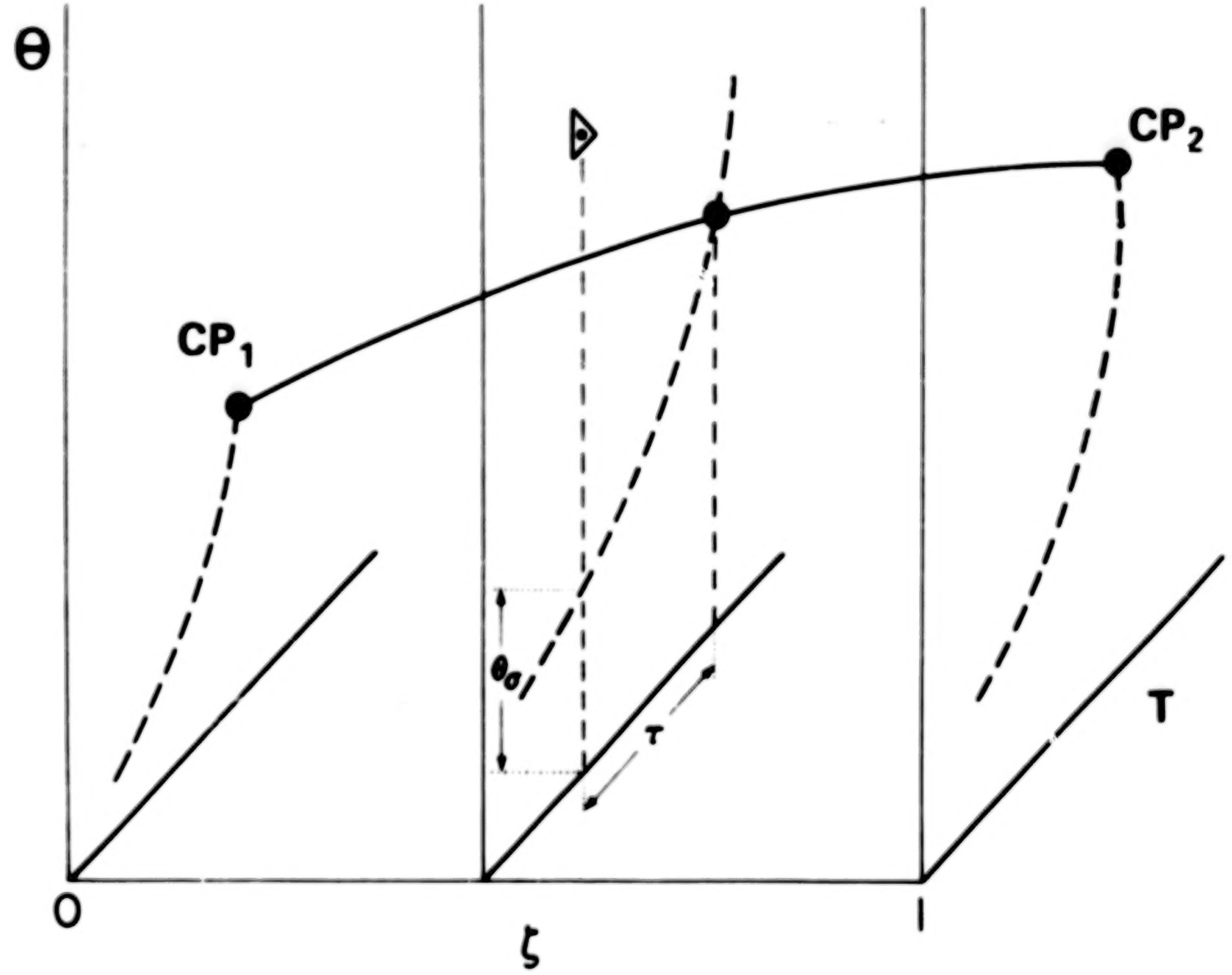

Figure 13. Independent field variables used in the Leung-Griffiths equation of state near the critical line of a binary gas-liquid system.

terminates in a point on the critical line but that can conceptually be extended into the one-phase region. For $\zeta = 0$ and $\zeta = 1$ this intersection reproduces the coexistence curves of the pure fluids 1 and 2, respectively. Leung and Griffiths now observe that the behavior of the mixture in the plane ζ = constant is completely analogous to the behaviour of a one-component fluid. In this plane a coordinate system can be chosen with coordinates $\tau = T - T_c(\zeta)$ and $h = \ln(\theta/\theta_\sigma)$, where $\theta_\sigma(\zeta,\tau)$ is the value of θ on the coexistence surface for the given values of ζ and τ. The variables τ and h are closely related to the variables ΔT^* and $\Delta\mu^*$ in the scaling laws for one-component fluids. In the formulation of Leung and Griffiths it is assumed that the pressure in the plane ζ = constant can be written as the sum of a regular background term $P_r(\zeta,\tau,h)$ which is an analytic function of its variables and a singular term $P_{sing}(\zeta,\tau,h)$ which satisfies the same scaling law in terms of τ and h as the singular part of the pressure of one-component fluids does in terms of ΔT^* and $\Delta\mu^*$ (cf. (3.31)). In addition P_{sing} contains a factor which is a smooth function of ζ so that one can interpolate between the scaled equations of state of two pure components.

The approach of Leung and Griffiths is an application of the geometric considerations outlined in the previous section. They applied it with success to describe the experimental equation of state data obtained by Wallace and Meyer [1972] near the critical line of mixtures of ^{3}He and ^{4}He. Doiron *et al.* [1976] showed that the same equation also is in good agreement with the experimental data of the pressure coefficient $(\partial P/\partial T)_{VX}$ for these mixtures. However, the cusp

like behavior of C_{VX} and $(\partial P/\partial T)_{VX}$, and the weak divergence of K_{TX}, predicted by the theory and incorporated in the equation of Leung and Griffiths, were not observed experimentally. Leung and Griffiths [1973] estimated that the cusp like behavior of C_{VX} and the divergence of K_{TX} would not be visible unless the critical line is approached to within 10^{-5} K. Outside this region, C_{VX} seems to diverge just as in pure fluids (Brown and Meyer, 1972) and K_{TX} appears to rise to a finite maximum (Wallace and Meyer, 1972).

The ^3He-^4He system has the simple feature that the critical line is a straight line connecting the critical points of the two pure components. Approximating the critical line by a quadratic curve D'Arrigo *et al.* (1975) applied the method of Leung and Griffiths to a mixture of CO_2 and C_2H_4 which exhibits critical azeotropy. They were able to describe the experimental dew and bubble curves satisfactorily. As discussed in Section 4.3, the theory of Griffiths and Wheeler predicts that K_{TX} will diverge weakly away from the critical azeotrope and strongly *at* the critical azeotrope. As in the case of the ^3He-^4He mixture it was found that these predicted anomalies in practice elude experimental observation, and it may be difficult to find systems in which they can be tested experimentally.

Moldover further generalized the method of Leung and Griffiths to systems in which the critical line is an arbitrary smooth curve connecting the critical points of the two pure components. He applied the method to the systems CO_2-C_2H_6, SF_6-C_3H_8 and C_3H_8-C_8H_{18} with satisfactory results (Moldover and Gallagher, 1976).

4.5 Critical Behavior Near the Consolute Point of Binary Liquids

The approach of Leung and Griffiths towards describing experimental data near a plait point is based on the continuity of critical phenomena in one- and two-component fluids. Thus, if universality of critical behavior is valid for one-component fluids, it is expected to extend to critical behavior in fluid mixtures as well.

The theory of Griffiths and Wheeler applies to all kinds of critical points in fluid mixtures, but the specific approach of Leung and Griffiths in its present form does not apply near the consolute point of partially miscible binary liquids. Nevertheless, a direct analogy can be made between critical phenomena near the gas-liquid critical point of a one-component fluid and critical phenomena near the critical mixing point of a binary liquid. When the pressure is held constant, the fundamental differential relation (4.4) for a binary mixture reduces to

$$d\mu_2 = -\tilde{s}dT - Xd\Delta. \tag{4.10}$$

Since the effect of pressure on critical mixing is small and since experiments in binary liquids usually are conducted with the vapor phase present, most experimental data may indeed be interpreted as obtained at constant pressure. On comparing (4.10) with the corresponding relation $-dP = -sdT-\rho d\mu$, given in (2.11) for one-component fluids, we conclude that the behavior of the fundamental equation $\mu_2(T,\Delta)$ for binary liquids at constant P near the critical mixing point will be analogous to that of $P(T,\mu)$ near the critical point of a one-component fluid. A number of thermodynamic properties exhibiting analogous

critical behavior are listed in Table XI. The concentration X is now the order parameter analogous to the magnetization of a ferromagnet near the Curie point and the density of a fluid near the gas-liquid critical point. It appears that the coexistence curve is considerably more symmetric when the concentration of either species is taken per unit of volume of the mixture rather than per unit of mole (Hildebrand *et al*, 1970). Therefore, the experimental data near the consolute critical point of a binary liquid are preferably analyzed with the concentration measured in terms of volume fractions.

Table XI

Analogy Between Critical Behavior of One-Component Fluids and Critical Mixing of Binary Liquids

	One-Component	Binary Liquid (P = Constant)
Fundamental Equation	$P(T,\mu)$	$\mu_2(T,\Delta)$
"Density"	$\rho = (\partial P/\partial \mu)_T$	$X = -(\partial \mu_2/\partial \Delta)_{T,P}$
Coexistence Curve	$\rho(T)$	$X(T)$
Equation of State	$\mu(\rho,T)$	$\Delta(X,T)$
Susceptibility (strongly divergent)	$\chi_T = (\partial^2 P/\partial \mu^2)_T$	$\chi_T = -(\partial^2 \mu_2/\partial \Delta^2)_{T,P}$
Specific Heat (weakly divergent)	$C_V/V = T(\partial^2 P/\partial T^2)_\rho$	$C_{P,X} = -T(\partial^2 \mu_2/\partial T^2)_{X,P}$

The critical exponents α, β, γ, δ now represent the power law behavior of C_{PX} as a function of temperature, the composition difference between the two coexisting phases as a function of temperature, the osmotic susceptibility χ_T as a function of temperature and the critical isotherm of μ_2 as a function of concentration. A power law analysis of coexistence curve data for nine binary liquids mixtures was made by Stein and Allen [1974]. A comprehensive review of critical exponent values found experimentally for binary fluids has been presented by Scott [1977]. When the coexistence curve data for various fluids were represented by a simple power law one most frequently deduced effective values for the exponent β between 0.33 and 0.35 (Stein and Allen, 1974; Scott, 1977). The experimental information concerning the exponents α and β of binary liquids is rather limited. Morrison and Knobler [1976] recently reported $0.08 \leq \alpha \leq 0.14$ for the isobutyric acid-water system.

Recently, experimental information has become available which does support the hypothesis of universality for binary liquid mixtures. Greer [1976] obtained a set of very accurate coexisting density data for the isobutyric acid-water system using a magnetic-float densimeter. After converting the data to volume fractions she found that the coexistence curve could be represented by a simple power law $B|\Delta t^*|^{\beta}$ in the range $|\Delta T^*| < 6 \times 10^{-3}$ with $\beta = 0.328 \pm 0.004$. She also showed that an analysis of the coexistence curve data reported by Gopal *et al.* [1973, 1974] for carbondisulfide-nitromethane in terms

of a 3-term Wegner expansion of the type presented in (3.37) yields a leading exponent $\beta = 0.316 \pm 0.008$. Earlier Balzarini [1974] had already noted that the exponent β of aniline-cyclohexane assumed the constant value $\beta = 0.328 \pm 0.007$ in a range $|\Delta T^*| < 10^{-2}$. The osmotic susceptibility $\chi_T = (\partial X/\partial \Delta)_{T,P}$ and, hence, the exponent γ can be determined by measuring the intensity of scattered light (Fabelinski, 1968). From a review of the light scattering data Chu [1972] suggested as the most probable value $\gamma = 1.23 \pm 0.02$. Recent light scattering measurements obtained by Chang *et al.* [1976] for 3-methylpentane-nitroethane at temperatures corresponding to $|\Delta T^*| < 3 \times 10^{-3}$ gave a value $\gamma = 1.240 \pm 0.014$. The close agreement between the exponent values currently found experimentally for β and γ of binary liquids with the values (2.78) calculated theoretically from the renormalization group theory does provide substantial evidence in support of the hypothesis of universality. The asymptotic power laws in binary liquids near the critical point appear to hold over a somewhat larger temperature range than in fluids near the gas-liquid critical point. Whether there exists a physical reason for this phenomenon or whether it is just the consequence of a fortuitous cancellation between the first few correction terms in the Wegner expansion is not clear yet.

Attempts have also been made to represent experimental chemical potential data of binary mixtures near the critical mixing point by a scaled equation of state analogous to (3.11) (Simon *et al.*, 1972). However, progress has been limited due to a lack of sufficient experimental data off the critical isochore and coexistence curve.

V. Critical Fluctuations

5.1 Correlation Function and Power Laws

When a system approaches a critical point, its thermodynamic states are accompanied by large fluctuations in the order parameter. Thus a fluid near the gas-liquid critical point exhibits large density fluctuations and a liquid mixture near the critical mixing point exhibits large concentration fluctuations. Here we shall develop an explicit description of these fluctuations in a fluid near the gas-liquid critical point. The corresponding equations for a binary liquid near the critical mixing point are obtained if the density is replaced with the concentration of either component.

The magnitude and spatial character of these fluctuations are described in terms of a correlation function defined as

$$\rho^2 G(|\vec{r}-\vec{r}'|) = \langle\{\rho(\vec{r})-\rho\}\{\rho(\vec{r}')-\rho\}\rangle = \langle\rho(\vec{r})\rho(\vec{r}')\rangle - \rho^2 , \qquad (5.1)$$

where the brackets $\langle\ \rangle$ indicate an equilibrium average over a grand canonical ensemble. $\rho(\vec{r})$ is the local number density at position $\vec{r}$ and $\rho = \langle\rho(\vec{r})\rangle$ is the average equilibrium density which is independent of the position $\vec{r}$ (not considering the presence of external forces such as gravity). The correlation function $G(|\vec{r}-\vec{r}'|)$ measures the joint probability of finding molecules in volume elements $d\vec{r}$ and $d\vec{r}'$ minus the

average number of pairs.[†] For an isotropic fluid this probability is only a function of the distance $|\vec{r}-\vec{r}'|$. The zeroth moment of the correlation function is related to the compressibility by the fluctuation theorem (De Boer, 1949)

$$k_B T \chi_T = \rho^2 \int d\vec{r} G(r) \ , \tag{5.2}$$

where $\chi_T = \rho^2 K_T$ is the symmetrized isothermal compressibility introduced in (2.1). The correlation function G is a function of $\Delta\rho^*$ and ΔT^* as well as of r. Whenever we want to indicate the dependence on the thermodynamic variables explicitly, we write $G(\Delta\rho^*,\Delta T^*; r)$ instead of $G(r)$.

A static structure factor may be defined as[††]

$$\chi(\Delta\rho^*,\Delta T^*; k) = \frac{\rho^2}{k_B T} \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} G(\Delta\rho^*,\Delta T^*; r) \ , \tag{5.3}$$

so that

$$\chi(\Delta\rho^*,\Delta T^*;0) = \chi_T(\Delta\rho^*,\Delta T^*) \ . \tag{5.4}$$

[†] In the literature the correlation function $G(|\vec{r}-\vec{r}'|)$ is usually defined such that $\rho^2 G(|\vec{r}-\vec{r}'|) + \rho\delta(\vec{r}-\vec{r}') = \langle\rho(\vec{r})\rho(\vec{r}')\rangle - \rho^2$, where the δ-function accounts for the self correlation at $\vec{r}' = \vec{r}$ (Hirschfelder *et al.*, 1954). Here we prefer to absorb this δ-function in the definition of $G(|\vec{r}-\vec{r}'|)$. Because of their long-range character the difference between the two correlation functions becomes irrelevant sufficiently close to the critical point.

[††] In the definition of the structure factor we have included a factor $k_B T$ so that χ has the same dimension as the symmetrized compressibility χ_T. This factor may for all practical purposes be identified with $k_B T_c$ in the region where the scaling laws apply, but may have to be treated more carefully when corrections to the asymptotic scaling laws are considered.

This structure factor as a function of the wave number k can be measured, since it is directly proportional to the intensity of scattered electromagnetic radiation as a function of scattering angle (Fabelinskii, 1968; McIntyre and Sengers, 1968). We find it also convenient to introduce a dimensionless structure factor χ^* defined as

$$\chi^* = \frac{p_c}{\rho_c^2}\chi \ . \tag{5.5}$$

The range of the correlation function and, hence, the spatial extent of the fluctuations is characterized by a correlation length ξ. It may be defined as

$$\xi^2 = \frac{1}{2d}\frac{\int \vec{dr}\ r^2 G(r)}{\int \vec{dr} G(r)} \ , \tag{5.6}$$

where d is the dimensionality of the system or, in terms of the structure factor,

$$\xi^2 = -\lim_{k\to 0}\left(\frac{\partial \ln \chi(k)}{\partial k^2}\right)_{\Delta\rho^*,\Delta T^*} \ . \tag{5.7}$$

The correlation length $\xi = \xi(\Delta\rho^*,\Delta T^*)$ is a function of density and temperature which diverges at the critical point. In particular along the critical isochore $\Delta\rho^* = 0$ and the coexistence curve $\Delta\rho^* = \Delta\rho^*_{cxc}$ it behaves as

$$\xi(0,\Delta T^*) = \xi_0(\Delta T^*)^{-\nu} \qquad (\Delta T^* \geq 0) \ , \tag{5.8a}$$

$$\xi(\Delta\rho^*_{cxc},\Delta T^*) = \xi_0'|\Delta T^*|^{-\nu'} \qquad (\Delta T^* \leq 0) \ , \tag{5.8b}$$

which defines the critical exponents ν and ν'.

Another exponent η is introduced to specify the nature of the dependence of the correlation function on the distance r. It is defined such that at the critical point $\Delta\rho^* = 0$, $\Delta T^* = 0$

$$G(0,0;r) \propto \frac{1}{r^{d-2+\eta}} \quad , \tag{5.9}$$

or, equivalently

$$\chi(0,0;k) \propto k^{\eta-2} \quad . \tag{5.10}$$

The exponent η is zero in the classical theory of Ornstein and Zernike (Fisher, 1964). However, the exponent η is known to be different from zero for the lattice models with short range interactions that have been solved theoretically. Series expansion estimates for the correlation function exponents of the 3-dimensional Ising model are (Moore *et al.*, 1969, Camp *et al.*, 1976)

$$\nu = 0.638 \pm \begin{matrix} 0.002 \\ 0.008 \end{matrix} \qquad \eta = 0.041 \pm \begin{matrix} 0.006 \\ 0.003 \end{matrix} \tag{5.11}$$

while the calculations of Baker *et al.* [1976] for the Landau-Ginzburg-Wilson model yield the values

$$\nu = 0.627 \pm 0.01 \quad , \quad \eta = 0.021 \pm 0.02 \tag{5.12}$$

Using some heuristic arguments Thompson [1976] proposed the formula

$$\nu = \frac{d+2}{4(d-1)} \qquad (d \leq 4) \tag{5.13}$$

which implies $\nu = 5/8$ for dimensionality $d = 3$.

5.2 Homogeneity Postulate for the Structure Factor

In formulating the homogeneity postulate for the thermodynamic properties in Section 3.2 we started from the observation that the chemical potential difference $\Delta\mu$ is an odd and the compressibility $\chi_T = \rho^2 K_T$ is an even function of the density $\Delta\rho^*$. We then expect from (5.3), (5.4) and (5.7) that also the structure factor $\chi(\Delta\rho^*,\Delta T^*;k)$ and the correlation length $\xi(\Delta\rho^*,\Delta T^*)$ will be symmetric functions of $\Delta\rho^*$ as they are in the lattice gas. Unfortunately, there exists very little experimental information concerning the density dependence of the structure factor and the correlation length of fluids (Thomas and Schmidt, 1963,1964; Chu and Lin, 1970 Lin and Schmidt, 1974a), but the scant available data are at least consistent with this assumption (Hanley *et al.*, 1976). We shall thus assume the symmetry properties

$$\begin{aligned} \chi(-\Delta\rho^*,\Delta T^*;k) &= \chi(\Delta\rho^*,\Delta T^*;k) \\ \xi(-\Delta\rho^*,\Delta T^*) &= \xi(\Delta\rho^*,\Delta T^*) \end{aligned} \tag{5.14}$$

to be valid for real fluids, but more accurate experimental information is desirable..

It is now postulated that the structure factor, for densities and temperatures sufficiently close to the critical point and for wave numbers k small relative to the inverse molecular interaction range, is a generalized homogeneous functions of its variables (Hankey and Stanley, 1972)

$$\chi^*(\lambda^{b_\rho}\Delta\rho^*,\lambda^{b_T}\Delta T^*;\lambda^{b_k}k) = \lambda\chi^*(\Delta\rho^*,\Delta T^*;k) \ . \tag{5.15}$$

This homogeneity property was first formulated by Kadanoff [1966] for

the correlation function of the Ising model. It follows from the renormalization group theory in the same manner as shown in Section 3.7 for the free energy (Niemeijer and Van Leeuwen, 1976). On evaluating (5.15) in the limit $k \to 0$, we see that the homogeneity postulate for the thermodynamic functions is recovered, if the exponents b_ρ and b_T are identified with

$$b_\rho = -\frac{a_\rho}{1-2a_\rho} = -\frac{\beta}{\gamma} = -\frac{1}{\delta-1}, \quad b_T = -\frac{a_T}{1-2a_\rho} = -\frac{1}{\gamma} . \tag{5.16}$$

Substitution of (5.15) into (5.7) yields after proper redefinition of the parameter λ

$$\xi(\lambda^{-b_\rho/b_k}\Delta\rho^*, \lambda^{-b_T/b_k}\Delta T^*) = \lambda\xi(\Delta\rho^*, \Delta T^*) . \tag{5.17}$$

Thus the correlation length ξ is a generalized homogeneous function of the thermodynamic variables $\Delta\rho^*$ and ΔT^* as we found earlier for the singular part of the thermodynamic properties. Along the critical isochore $\Delta\rho^* = 0$ and along the coexistence curve $\Delta\rho^*_{cxc} = \pm B|\Delta T^*|^\beta$ we find in analogy with (2.45) and (2.46)

$$\xi(0, \Delta T^*) = \xi(0,1)(\Delta T^*)^{-b_k/b_T} \qquad (\Delta T^* \geq 0) ,$$

$$\xi(\Delta\rho^*_{cxc}, \Delta T^*) = \xi(B,-1)|\Delta T^*|^{-b_k/b_T} \qquad (\Delta T^* \leq 0) .$$

We thus recover the power laws (5.8) with

$$\nu = \nu' = b_k/b_T \tag{5.18}$$

The homogeneity postulate (5.13) reads in terms of the exponents β, γ, ν adopted for the power laws

$$\chi(\gamma^{-\beta/\gamma}\Delta\rho^*,\lambda^{-1/\gamma}\Delta T^*;\lambda^{-\nu/\gamma}k) = \lambda\chi(\Delta\rho^*,\Delta T^*;k) \ . \qquad (5.19)$$

Taking $\lambda^{\nu/\gamma} = k$, we conclude that at the critical point $\chi(0,0;k) = k^{-\gamma/\nu}\chi(0,0,1)$. Comparison with (5.10) yields the exponent relation (Fisher, 1964)

$$\boxed{\gamma = \nu(2-\eta)} \ . \qquad (5.20)$$

5.3 Scaling Laws and Hypothesis of Three-Scale Factor Universality

A generalized homogeneous function of three variables can be scaled to become a function of only two variables. To deduce a scaling law for the structure factor we take $\lambda^{\beta/\gamma} = \Delta\rho^*$ in (5.19) and obtain

$$\chi^*(\Delta\rho^*,\Delta T^*;k) = |\Delta\rho^*|^{-\gamma/\beta}\chi^*(1,x;y) \ , \tag{5.21}$$

where $x = \Delta T^*/|\Delta\rho^*|^{1/\beta}$ is the thermodynamic scaling variable introduced earlier and $y = k|\Delta\rho^*|^{-\nu/\beta}$ a new scaling variable. In the limit $k \to 0$

$$\chi^*(\Delta\rho^*,\Delta T^*;0) = |\Delta\rho^*|^{-\gamma/\beta}D^{-1}X(x/x_o) \ , \tag{5.22}$$

where $X(x/x_o) = \{\delta h(x/x_o) - (x/\beta x_o)h'(x/x_o)\}^{-1}$ is the scaling function for the isothermal compressibility introduced in Table VII.

The correlation length ξ satisfies a scaling law which may be written in the form

$$\xi(\Delta\rho^*,\Delta T^*) = |\Delta\rho^*|^{-\nu/\beta}\xi_{o,c}\Xi(x/x_o) \ , \tag{5.23}$$

where, in accordance with (5.7)

$$\{\xi_{o,c}\Xi(x/x_o)\}^2 = -\lim_{y\to 0}\frac{\partial \ln\chi^*(1,x;y)}{\partial y^2} \ . \tag{5.24}$$

The factor $\xi_{o,c}$ is the amplitude of the power law for the correlation length along the critical isotherm

$$\xi(\Delta\rho^*,0) = \xi_{o,c}|\Delta\rho^*|^{-\nu/\beta} \qquad (\Delta T^* = 0) \ . \tag{5.25}$$

It follows from (5.22) and (5.23) that the scaling law (5.21) for the structure factor also can be written in the form

$$\chi^*(\Delta\rho^*,\Delta T^*;k) = \chi_T^*(\Delta\rho^*,\Delta T^*)Y(\frac{x}{x_o};k\xi) \quad . \tag{5.26}$$

This formulation has the advantage that the new scaling function $Y(u,v)$ satisfies the boundary conditions

$$\lim_{v\to 0} Y(u;v) = 1 \quad , \tag{5.27a}$$

$$\lim_{v\to 0} \frac{\partial^2 Y(u;v)}{\partial v^2} = -1 \quad . \tag{5.27b}$$

Alternate forms for the scaling law of the structure factor are

$$\begin{aligned} \chi^*(\Delta\rho^*,\Delta T^*;k) &= \xi^{2-\eta}\Phi_\chi(\frac{x}{x_o};k\xi) \\ \chi^*(\Delta\rho^*,\Delta T^*;k) &= k^{\eta-2}\Psi_\chi(\frac{x}{x_o},k\xi) \quad , \end{aligned} \tag{5.28}$$

where the functions $\Phi_\chi(x/x_o;k\xi)$ and $\Psi_\chi(x/x_o;k\xi)$ can be readily related to the scaling functions introduced above.

The structure factor can be determined experimentally as a function of ξ and k by measuring the intensity of scattered light as a function of temperature and scattering angle. The wave number k is related to the scattering angle θ by the Bragg condition $k = 2k_o\sin(\theta/2)$, where k_o is the wave number of the incident light. If the observed scattered light intensity $I(k) \propto \chi(k)$, divided by the extrapolated intensity $I(0)$ at zero scattering angle, is plotted as a function of $k\xi$, it follows from the scaling law (5.26) that data obtained along a curve of constant x, such as the critical isochore, critical isotherm or coexistence curve, should collapse onto one single curve. In Fig. 14

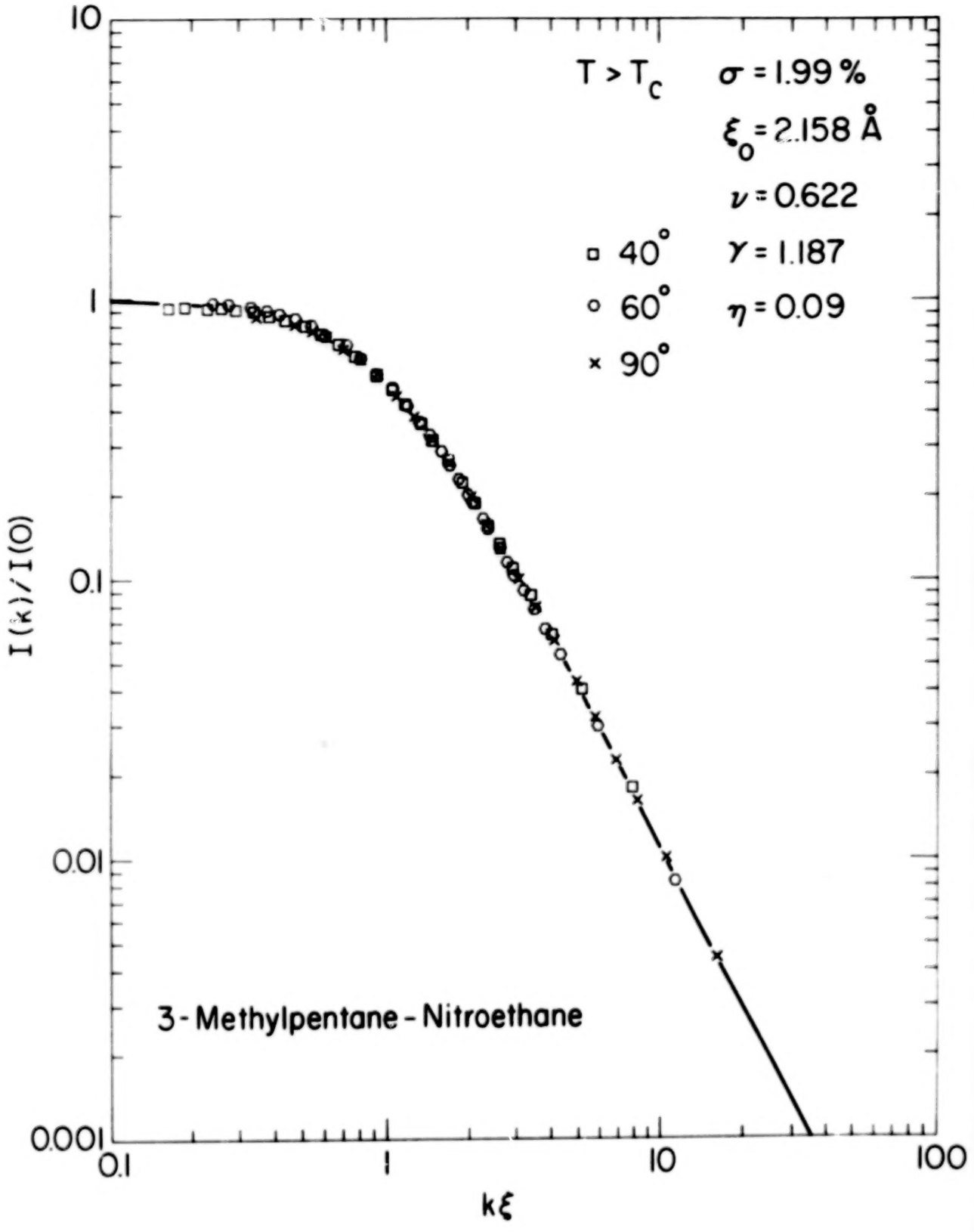

Figure 14. Scattered light intensity ratio I(k)/I(0) for 3-methylpentane-nitroethane at the critical concentration as a function of kξ.

we present an example of such a plot based on light scattering data obtained at three scattering angles (40°, 60°, 90°) for the binary liquid 3-methylpentane-nitroethane at the critical concentration as a function of temperature (Chang *et al.*, 1972).

In Sections 2.7 and 3.5 we formulated the hypothesis of universality of thermodynamic behavior near the critical point. This same principle, when extended to the correlation function, asserts that for all systems which differ only with respect to irrelevant parameters in their Hamiltonians, the scaling function $\chi^*(1,x;y)$ introduced in (5.21) will be the same, except for three adjustable factors which define the scale of χ^*, x and y (Kadanoff, 1971; Ferer and Wortis, 1972). For these scale factors we may choose the power law amplitudes D, x_o and $\xi_{o,c}$ (or ξ_o). Thus the hypothesis of three-scale-factor universality predicts that not only the function $h(x/x_o)$ introduced in (3.11) for the equation of state, but also the scaling functions $Y(x/x_o;k\xi)$ and $\Xi(x/x_o)$ for the structure factor and correlation length wil be the same for all systems within one universality class.

5.4 Correlation Scaling Function and Correlation Function Exponent Values

In order to deduce the correlation function exponents ν and η and the correlation length ξ from experimental data and to make a quantitative analysis of the universality hypothesis, one needs an explicit functional form for the correlation scaling function $Y(x/x_o;y)$ as a function of $y = k\xi$. For small values of y the inverse scaling function has a Taylor series expansion in terms of y^2 (Fisher, 1964)

$$Y^{-1}(x/x_o;y) = 1 + y^2 + O(y^4) \ , \ (y << 1) \ , \tag{5.29}$$

where the first two terms follow from the boundary conditions (5.27). For very large values of the variable y the scaling function Y is expected to have the form (Fisher and Langer, 1968; Stell, 1968; Brézin *et al.*, 1974a,b; Fisher and Aharony, 1974).

$$Y(\frac{x}{x_o};y) = \frac{C_1(x/x_o)}{y^{2-\eta}} \left[1 + \frac{C_2(x/x_o)}{y^{(1-\alpha)/\nu}} + \frac{C_3(x/x_o}{y^{1/\nu}}\right], \quad (y >> 1), \tag{5.30}$$

where C_1, C_2 and C_3 are (universal) functions of the thermodynamic scaling variable x/x_o.

The early experimental light scattering work has often been interpreted using either the Ornstein-Zernike scattering function

$$Y_{OZ} = \frac{1}{1+y^2} \ , \tag{5.31}$$

or the simple Fisher scattering function

$$Y_F = \frac{1}{(1+y^2)^{1-\eta/2}} \tag{5.32}$$

for all values of y (Calmettes et al., 1972; Chu, 1972; Lai and Chen, 1972; Volochine, 1972). However, the Ornstein-Zernike scattering function implies that $\eta = 0$ which is known to be incorrect from the theoretical model results, while the simple Fisher scattering function (5.32) cannot accommodate simultaneously the correct amplitudes of the leading terms in the small and large y expansions. A proposed scattering function is not satisfactory unless it provides a method of interpolating between the asymptotic forms (5.29) and (5.30). The problem is compounded by the fact that the scaling function Y is not only a function of $k\xi$, but also

of the thermodynamic scaling variable x/x_o. In practice one tries to formulate a scattering function that accommodates the known numerical results for the 2- and 3-dimensional Ising model.

For the 3-dimensional Ising model Tarko and Fisher [1975] proposed

$$Y_{TF}(\frac{x}{x_o};y) = \frac{(1+\phi^2y^2)^{\eta/2}}{1+\psi y^2}\left[1 - \Lambda + \Lambda\frac{(1+\tfrac{1}{4}\psi y^2)}{2\ln\Omega} - \ln\left(\frac{\Omega^2+\tfrac{1}{4}\psi y^2}{1+\tfrac{1}{4}\psi y^2}\right)\right], \qquad (5.33)$$

where the parameters Φ, Λ and Ω are (universal) functions of x/x_o and where

$$\psi(\frac{x}{x_o}) = \frac{1+\tfrac{1}{2}\eta\phi^2}{1-\tfrac{1}{4}\Lambda\{1-(\Omega^2-1)/2\Omega^2\ln\Omega\}}.$$

Taking $\Lambda(\infty) = 0$, this form reduces at the critical isochore $x = \infty$ to (Fisher and Burford, 1967)

$$Y_{FB}(\infty;y) = \frac{\{1+\phi^2(\infty)y^2\}^{\eta/2}}{1+\psi(\infty)y^2}, \qquad (5.34)$$

where $\psi(\infty) = 1 + \tfrac{1}{2}\eta\phi^2(\infty)$. For large values of y the leading term in the asymptotic expansion (5.30) is recovered with $C_1(\infty) = \phi^{\eta}(\infty) / \{1+\tfrac{1}{2}\eta\phi^2(\infty)\}$. However, the Fisher-Burford and Tarko-Fisher scattering functions (5.34) and (5.33) still do not reproduce the higher order terms in the asymptotic expansion (5.30). A quantitative analysis of the limitations of these scattering functions by testing them on the exactly-solved 2-dimensional Ising model was made by Tracy and McCoy [1975]. Lin and Schmidt [1974a) have analyzed their X-ray scattering data for argon near the critical point in terms of the Fisher-Burford and Tarko-Fisher

scattering functions. Swinney and Saleh [1973] evaluated the effect of the Fisher-Burford scattering function on the theoretical expression for the decay rate of the order parameter in fluids. Tartaglia and Thoen [1975] tried to discriminate between the various scattering functions from an analysis of sound absorption and dispersion data near the critical point of xenon.

Recently, Bray [1976] proposed a scattering function which in two dimensions does reproduce the known Ising model values for all $k\xi$ to within 0.03%. It was obtained by modifying an earlier scattering function of Ferrell and Scalapino [1975] so as to incorporate the Fisher-Langer form (5.30) for large values of $y = k\xi$. For the 3-dimensional Ising model in zero field which corresponds to the critical isochore of the lattice gas, this scattering function is defined through the equations

$$Y^{-1}(\infty;y) = 1 + y^2 f(\frac{y^2}{9})/f(-1/9) \tag{5.35a}$$

$$f(z) = \frac{2}{\pi}\sin(\frac{\pi\eta}{2})\int_{w_o}^{\infty}\frac{dw}{w^{\eta}}\frac{wF(w)}{w^2+z} \quad , \tag{5.35b}$$

$$F(w) = \frac{P+Q\,\mathrm{cotg}\,(\frac{\pi\eta}{2})}{P^2+Q^2} \quad , \tag{5.35c}$$

with

$$P(w) = 1 - \frac{C_2}{(3w)^{(1-\alpha)/\nu}}\sin(\frac{\pi}{2\nu}) + \frac{C_3}{(3w)^{1/\nu}}\cos(\frac{\pi}{2\nu}) ,$$

$$Q(w) = \frac{C_2}{(3w)^{(1-\alpha)/\nu}}\cos(\frac{\pi}{2\nu}) - \frac{C_3}{(3w)^{1/\nu}}\sin(\frac{\pi}{2\nu}) .$$

The constants C_2 and C_3 are to be identified with the coefficients $C_2(\infty)$

and $C_3(\infty)$ in the Fisher-Langer form (5.30) for large values of y and must be the same for all systems within one universality class. The integration cut-off constant w_o in (5.35b) is related to the coefficient $C_1(\infty)$ by the condition

$$C_1(\infty) = 3^{-\eta} f(-1/9) \ . \tag{5.35d}$$

The value of this coefficient estimated from series expansions for the 3-dimensional Ising model is 0.90 ± 0.01 (Ritchie and Fisher, 1972).

Many light scattering data and X-ray scattering data are obtained under conditions for which $k\xi << 1$. One may then neglect the higher order terms in the expansion (5.29) and analyze the data in terms of

$$\chi(k) = \frac{\chi(0)}{1+k^2\xi^2} \tag{5.36}$$

Thus if the inverse scattering intensity $I^{-1}(k) \propto \chi^{-1}(k)$ is plotted as a function of k^2, at each temperature and density the data will fall on a straight line whose intercept is proportional to the inverse compressibility $\chi^{-1}(0)$ while the ratio of slope over intercept yields the correlation length ξ^2. Such a plot is usually referred to as an Ornstein-Zernike plot. According to the Ornstein-Zernike theory the data would follow a straight line for all values of $k\xi$; since the exponent of η is small the deviations from linear behavior observed in real fluids are very small. We show examples of such O-Z plots in Fig. 15 for carbon dioxide near the critical point based on X-ray scattering data (Chu and Lin, 1970) and in Fig. 16 for the binary liquid 3-methylpentane-nitroethane near the critical mixing point based on light scattering data (Wims, 1967; McIntyre and Sengers, 1968).

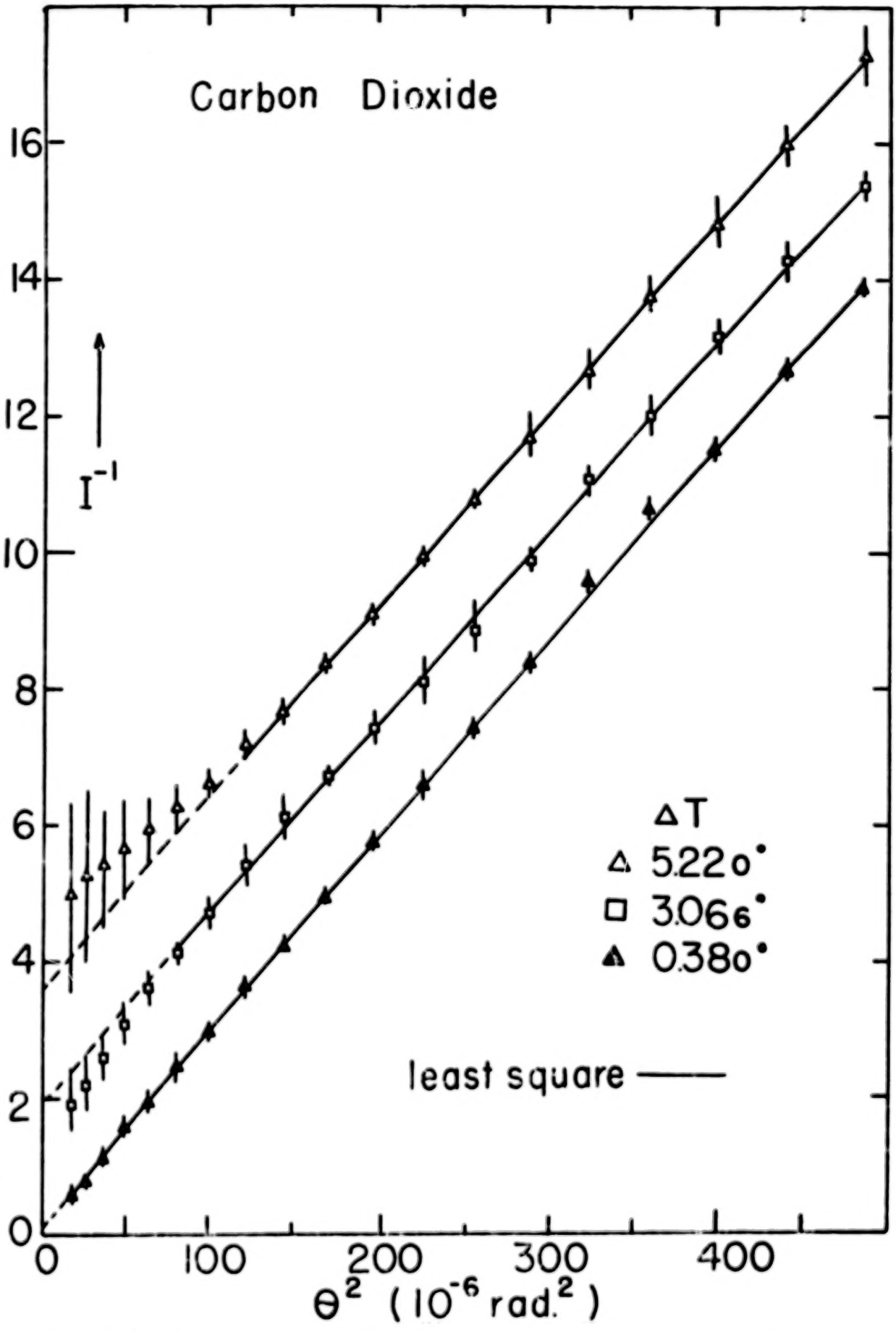

Figure 15. Reciprocal relative scattering intensity as a function of $(k/k_o)^2 \approx \theta^2$ for carbon dioxide at the critical density and at various values of $\Delta T = T - T_c$ (Chu and Lin, 1970).

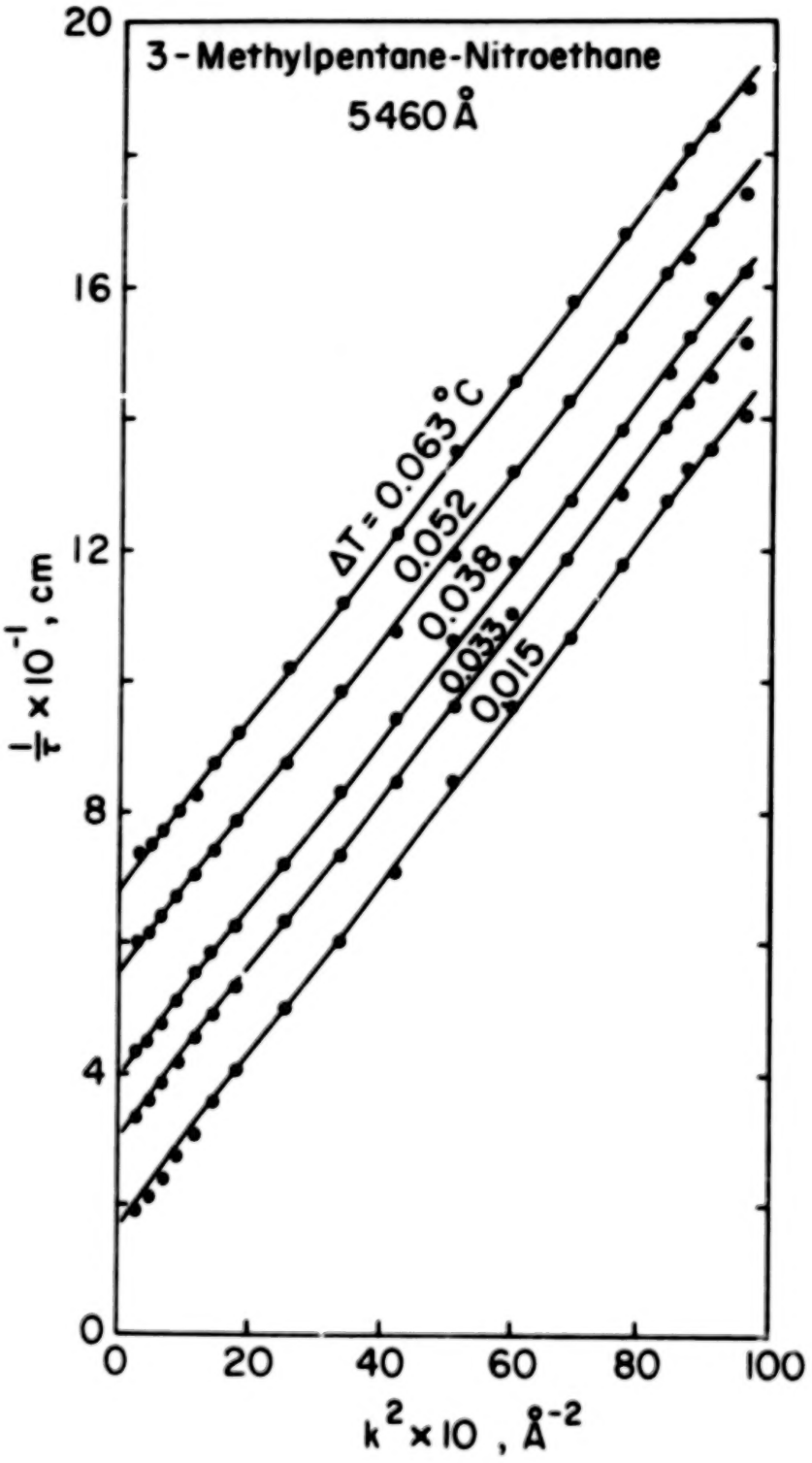

Figure 16. Inverse scattering intensity in turbidity units as a function of k^2 for 3-methylpentane-nitroethane at the critical concentration and at various values of $\Delta T = T - T_c$ (McIntyre and Sengers, 1968).

The correlation length has been determined experimentally for such gases as ^{3}He (Ohbayashi and Ikushima, 1975), ^{4}He (Tominaga, 1974; Kagoshima *et al.*, 1973), Ar (Lin and Schmidt, 1974a), Xe (Smith *et al.*, 1971), CO_2 (Chu and Lin, 1970; Lunacek and Cannell, 1971), SF_6 (Puglielli and Ford, 1970; Cannell, 1975) and for a number of binary liquids reviewed by Chu [1972], Anisimov [1975] and Scott [1977]. In interpreting the experimental results one must realize that there exists a strong correlation between the exponent ν and the amplitude ξ_o of the power law (5.8). Although a variety of values have been reported for the exponent ν the more reliable data are all consistent with $\nu = 0.63 \pm 0.02$ for gases as well as binary liquids.

Having determined in addition the exponent γ from the zero-angle scattering data $\lim_{k\to 0} \chi(k)$, one may then infer a value for the exponent from the Fisher relation (5.20). Typical values thus obtained are $\eta = 0.07 \pm 0.04$ for CO_2 (Lunacek and Cannell, 1971) and $\eta = 0.03 \pm 0.03$ for SF_6 (Cannell, 1975), but they are obviously very sensitive to the values adopted for γ and ν.

In order to obtain more detailed information one needs to measure the intensity of scattered light over a larger range of $k\xi$ values. For a given wave length and a given range of scattering angles this can be done in principle by approaching the critical point more closely. However, here one runs into major complications due to multiple scattering and attenuation of the light beam (Chalyi, 1969; White and Maccabee, 1971; Oxtoby and Gelbart, 1974; Bray and Chang, 1975; Boots *et al.*, 1976; Moldover *et al.*, 1976).

As an alternative one can use X-ray scattering or neutron scattering which probe the fluctuations at larger values of k. From neutron scattering experiments Warkulwiz *et al.* [1974] reported a value $\eta = 0.11 \pm 0.03$ for neon and from X-ray scattering experiments data Lin and Schmidt [1974b] deduced a value $\eta = 0.10 \pm 0.05$ for argon. However, there exists some doubt as to whether the structure factor can still be represented by the simple scaling law (5.26) without correction terms at the values of k covered by these experiments (Mozer, 1976; Schmidt, 1976).

Very recently Chang *et al.* [1976] obtained an accurate set of light scattering data for the system 3-methylpentane-nitroethane. This system has a relatively small scattering cross section and they were able to cover a range $0.18 < k\xi < 26$ with only minor corrections for double scattering and turbidity. The data could be well represented by the scattering function (5.35) with the parameters $C_2 = 1.773$, $C_3 = -2.745$, $w_o = 1$ and the exponent values

$$\nu = 0.625 \pm 0.005 , \quad \eta = 0.016 \pm 0.014 \tag{5.37}$$

These values are in good agreement with the exponent values (5.12) calculated by Baker *et al.* [1976] and support the validity of the universality hypothesis for the correlation function. It appears that the critical exponent values (2.78) and (5.12) calculated theoretically from the Landau-Ginzberg-Wilson model are in slightly better agreement with the experimental data for fluids than the estimates (2.64) and (5.11) deduced from series expansions for the 3-dimensional Ising model.

5.5 Hyperscaling Relations

The hypothesis of universality has its origin in the long range character of the fluctuations. Since in the critical region the correlation length ξ becomes much larger than the range of the molecular interaction, it is expected that the singular nature of the cooperative phenomena become independent of the detailed shape of the molecules. The correlation length ξ was defined in (5.6). For distances much smaller than ξ the density fluctuations are highly correlated, while for distances much larger than ξ the density fluctuations become uncorrelated. Hence, the correlation length ξ may be visualized as the radius of droplet-like conglomerates referred to as clusters (Widom, 1974).

The singular thermodynamic behavior is characterized by two critical exponents among the thermodynamic exponents α, β, γ and δ. The long-range behavior of the correlation function is characterized by the two exponents ν and η. If the singular behavior of the system is completely determined by the long-range character of the correlation function, one would expect that the thermodynamic exponents are related to the correlation function exponents. One such a relation is the Fisher relation $\gamma = \nu(2-\eta)$. However, a second relation is needed to relate the thermodynamic exponents and the correlation function exponents uniquely. Such a relation may be obtained by an argument first proposed by Widom [1965b,1974].

The energy associated with the spontaneous density fluctuations that extend over a distance ξ will be of order $k_B T \approx k_B T_c$. Hence the free energy density associated with these fluctuations will be of order $k_B T_c/\xi^d$. One expects this energy to be solely responsible for the singular contribution A_{sing}/V to the Helmholtz free energy density. Thus $A_{sing}/V = P_c A^*_{sing}$ (cf. (2.2)) is assumed to be proportional to $k_B T_c/\xi^d$.

It is convenient to introduce the dimensionless quantity

$$Q^d \equiv \frac{|A_{sing}/V|\xi^d}{k_B T_c} = \frac{P_c |A^*_{sing}|\xi^d}{k_B T_c} , \tag{5.38}$$

which, according to Widom's arguments, is expected to remain finite at the critical point. Since along each curve of fixed $x = \Delta T^*/|\Delta\rho^*|^{1/\beta}$, A^*_{sing} varies as $|\Delta T^*|^{2-\alpha}$ and ξ as $|\Delta T^*|^{-\nu}$, this assumption implies the exponent relation

$$d\nu = 2-\alpha . \tag{5.39}$$

When this relation is combined with the other exponent relations one also obtains (Fisher, 1967a; Stell, 1970)

$$\frac{2-\eta}{d} = \frac{\delta-1}{\delta+1} . \tag{5.40}$$

The relations (5.39) and (5.40) are sometimes referred to as hyperscaling relations. They contain the dimensionality d and are expected to be valid in those dimensions ($d \leq 4$) where the correlation function becomes sufficiently long range. The hyperscaling relations are satisfied for the 3-dimensional Ising model. The validity of the hyperscaling relations in two and three dimensions is implicitly assumed in the renormalization group theory of critical phenomena. Hence they are automatically satisfied by the numerical estimates (2.78) and (5.12) for the Landau-Ginzburg-Wilson model. The problem is, however, that they are not satisfied within error by the series expansion estimates for the 3-dimensional Ising model (Baker, 1976). The origin of this discrepancy has not yet been resolved. The hyperscaling relations

are satisfied by the fluid critical exponents within the accuracy with which they are currently known experimentally.

5.6 Hypothesis of Two-Scale-Factor Universality

According to the hypothesis of universality formulated in Section 5.3, the scaling function for the structure factor is a universal function of the scaling variables $\Delta T^*/|\Delta\rho^*|^{1/\beta}$ and $k|\Delta\rho^*|^{-\gamma/\beta}$ except for three scale factors D, x_o and $\xi_{o,c}$. The number of independent scale factors can be further reduced by the hypothesis of two-scale-factor universality. It follows from the assertion, proposed by Stauffer, Ferer and Wortis [1972], that the dimensionless quantity Q, defined in (5.38) is a universal function $Q(x/x_o)$ of the thermodynamic scaling variable x/x_o; that is, along any given curve x/x_o = constant, the quantity Q should assume the same value for all systems within one universality class. If we now substitute into (5.38) the scaled expressions $A^*_{sing} = |\Delta\rho^*|^{(2-\alpha)/\beta} D a(x/x_o)$ and $\xi = |\Delta\rho^*|^{-\nu/\beta}\xi_{o,c}\Xi(x/x_o)$ in accordance with (3.10) and (5.23), and assume the validity of the hyperscaling relations, this hypothesis of universal $Q(x/x_o)$ implies

$$\frac{P_c}{k_B T_c} D\xi^d_{o,c} = \text{universal constant} , \tag{5.41}$$

yielding a relation between the scale factors D and $\xi_{o,c}$. The hypothesis of two-scale-factor universality does follow from the renormalization group theory as recently shown by Hohenberg *et al.* [1976].

Since the Helmholtz free energy density is usually not measured directly, the assumption is often restated in terms of the specific heat density C_V/V. Universality of Q implies that also the combination

$\xi^d|\Delta T^*|^2 C_V/V$ is universal. Empirical evidence in support of this hypothesis for fluids was presented by Bauer and Brown [1975].

In principle, the hypothesis of two-scale-factor universality could be investigated by comparing the experimental data for C_V and for different fluids at the same $\Delta\rho^*$ and ΔT^* without taking recourse to a power law analysis (Stauffer *et al.*, 1972; Bauer and Brown, 1975). Here, however, we investigate the relations between the power law amplitudes implied by the hypothesis. In the absence of experimental data for the correlation length amplitude $\xi_{o,c}$ along the critical isotherm, we consider the value of Q along the critical isochore $x = \infty$

$$Q(\infty) = \left\{\frac{P_c}{k_B T_c} \frac{A^+}{(2-\alpha)(1-\alpha)\alpha}\right\}^{1/3} \xi_o = \text{constant} , \qquad (5.42a)$$

or, in terms of the constants of the parametric equations of state in Table VIII

$$Q(\infty) = \left\{\frac{P_c}{k_B T_c} ak|f_o|\right\}^{1/3} \xi_o = \text{constant} . \qquad (5.42b)$$

The hypothesis of two-scale-factor universality presupposes that the experimental data for different fluids can be represented by a power law with universal exponents. As discussed in Section 3.8 the range of simple asymptotic behavior of fluids near the gas-liquid critical point is restricted to $|\Delta T^*| < 10^{-4}$. In this range insufficient experimental correlation length data are available to investigate the validity of the hypothesis with any precision.

We have evaluated the quantity $Q(\infty)$ for a number of gases in an extended temperature range using the effective fluid exponents (3.29) adopted in Table X. The results are presented in Table XII. The free

energy amplitude akf_o was calculated from the parameters presented in Table X. Substitution of the effective thermodynamic exponents (3.29) into the hyperscaling relation (5.39) yields an effective value $\nu = 0.633$ for the correlation length exponent ν. Estimates for the corresponding correlation length amplitude ξ_0 were obtained as follows. For ^{4}He and Ar we took the values reported by Tominaga [1974] and by Lin and Schmidt [1974a], respectively. For Xe we took $\xi_o = (2.0 \pm 0.2)$ Å based on the data of Smith *et al.* [1971] as reinterpreted by Swinney and Henry [1973]. A reanalysis of the X-ray scattering data of Chu and Lin [1970] for CO_2 yields $\xi_o = (1.6 \pm 0.1)$ Å, while Lunacek and Cannell [1971] report $\xi_o = (1.50 \pm 0.09)$ Å. From the work of Cannell [1975] we estimate for SF_6 $\xi_o = (1.9 \pm 0.1)$ Å, but there are some differences with the data of Puglielli and Ford [1970]. In no case is the correlation length on an absolute basis known with an accuracy better than 10%, so that we

Table XII

Test of Two-Scale-Factor Universality for Gases

	$(P_c/k_B T_c)^{1/3}$ Å^{-1}	$(akf_o)^{1/3}$	ξ_o Å	Ω (∞)
^{4}He	0.1470	1.46	2.2 ± 0.6	0.47 ± 0.13
Ar	0.1327	2.15	1.7 ± 0.2[5]	0.48 ± 0.07
Xe	0.1135	2.15	2.0 ± 0.2	0.49 ± 0.05
CO_2	0.1207	2.44	1.55± 0.1	0.46 ± 0.03
SF_6	0.0949	2.42	1.9 ± 0.1	0.45 ± 0.03

cannot expect to check two-scale-factor universality better than to within 10%. Nevertheless, it appears from Table XII that the quantity $Q(\infty) = 0.46 \pm 0.04$ is remarkably constant for these five gases. The hypothesis of two-scale-factor universality would thus appear to be consistent with the current experimental evidence. The corresponding value of $Q(\infty)$ for the 3-dimensional Ising model is 0.43 (Stauffer *et al.*, 1972), but such a comparison is of dubious value since we have used exponent values that differ from those of the Ising model.

5.7 Correlation Length and Equation of State

If we adopt the effective universal value $Q(\infty) = 0.46$ for all gases, we can predict an effective value for the correlation length amplitude ξ_0 from the equation of state parameters presented in Table X. The values thus estimated for ξ_0 are given in the last column of Table X. In order to calculate the correlation length at densities other than the critical density we need to formulate a functional form for the scaling function $\Xi(x/x_0)$ introduced in (5.23). For the 3-dimensional Ising model this question has been considered by Tarko and Fisher [1975]

In analogy to the formulation used for the singular contributions to the thermodynamic properties, the required analyticity properties of ξ in the one-phase region away from the critical point can be automatically ensured by a parametric representation

$$\begin{aligned} \Delta T^* &= r(1-b^2\theta^2) \quad , \\ \Delta\rho^* &= kr^\beta\theta(1+c\theta^2) \quad , \\ \xi &= \xi_0 r^{-\nu} g(\theta) \quad , \end{aligned} \tag{5.43}$$

where $g(\theta)$ is an analytic function of θ which must be even in θ. The case $c = 0$ corresponds again to the linear model and the case $c \neq 0$ corresponds again to the cubic model. In order to reproduce the correct power law amplitudes along the critical isochore and the coexistence curve, the function $g(\theta)$ must satisfy the boundary conditions

$$g(0) = 1 \quad , \quad g(\pm 1) = \xi_o'/\xi_o \quad . \tag{5.44}$$

For the 3-dimensional Ising model $\xi_o'/\xi_o = 0.51$ (Tarko and Fisher, 1975). For fluids the ratio ξ_o'/ξ_o is only known with very limited accuracy. The most careful study of this ratio was made by Lin and Schmidt [1974c] with the result $\xi_o'/\xi_o = 0.49 \pm 0.05$. For ^{4}He Tominaga [1974] reported $\xi_o'/\xi_o = 0.45 \pm 0.1$.

A more practical approach is to relate the correlation length to the isothermal compressibility. It follows from (5.20) and (5.23) that the correlation length can be written in the form

$$\xi = \xi_o R(\theta) \, (\Gamma^{-1} \chi_T^*)^{1/2-\eta} \quad , \tag{5.45}$$

where R is a universal function of x/x_o and, hence, a universal function of the parametric variable θ. On the critical isochore and coexistence curve it is equal to

$$R(0) = 1 \; , \; R(\pm 1) = \frac{\xi_o'}{\xi_o} \left(\frac{\Gamma}{\Gamma'} \right)^{1/2-\eta} \quad . \tag{5.46}$$

For the 3-dimensional Ising model $R(\pm 1) = 1.17$ (Tarko and Fisher, 1975). The proportionality constant between ξ and $\chi_T^{*1/2-\eta}$ along the critical isochore and coexistence curve of argon was determined by Lin and

Schmidt [1974a] with a precision of about one percent; from their work we conclude $R(\pm 1) = (4.04 \pm 0.05)/(3.45 \pm 0.03) = 1.17 \pm 0.03$ in good agreement with the theoretical value $R(\pm 1) = 1.17$ for the Ising model. The simplest polynomial accommodating this boundary condition would be

$$R(\theta) = 1 + 0.17\theta^2 \ . \tag{5.47}$$

In practical calculations of the correlation length of fluids $R(\theta)$ is usually assumed to be independent of θ. In this approximation

$$\xi = \xi_o(\Gamma^{-1}\chi_T^*)^{1/2-\eta}, \tag{5.48}$$

which for the restricted cubic model reduces to

$$\xi = \xi_o r^{-\nu} \ . \tag{5.49}$$

This assumption is not strictly correct as suggested by the Ising model and confirmed by the work of Lin and Schmidt. The approximate equation (5.48) reproduces correctly the behavior of the correlation length along the critical isochore, but not along the coexistence curve. When it is used in conjunction with the equation of state parameters given in Table X, it yields $\xi_o'/\xi_o = (\Gamma'/\Gamma)^{1/(2-\eta)} = 0.46$ which is 10% lower than the corresponding value for the Ising model, but well within the precision with which this ratio is currently known experimentally for fluids.

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